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Driver detection of water quality trends in three large European river basins

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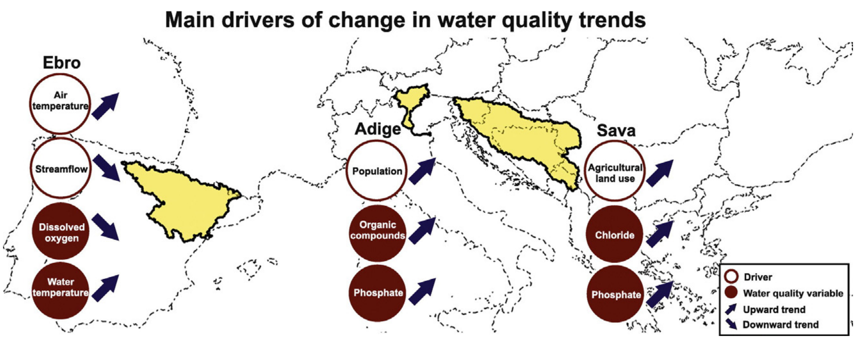
HIGHLIGHTS

- Trend analysis of physico-chemical variables in surface waters and their drivers of change
- Comparison among surficial water quality in three contrasting European river basins
- Highest risk of developing anoxic conditions in Iberian Peninsula
- Agriculture as source of organic compounds and phosphate in the Adige basin
- Increasing trends of chloride and phosphate in the Sava linked with agriculture

GRAPHICAL ABSTRACT



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ABSTRACT

This study analyses how indicators of water quality (thirteen physico-chemical variables) and drivers of change (i.e., monthly aggregated air temperature and streamflow, population density, and percentage of agricultural land use) coevolve in three large European river basins (i.e., Adige, Ebro, Sava) with different climatic, soil and water use conditions. Spearman rank correlation, Principal Component Analysis, and Mann-Kendall trend tests were applied to long-term time series of water quality data during the period 1990–2015 in order to investigate the relationships between water quality parameters and the main factors controlling them. Results show that air temperature, considered as a proxy of climatic change, has a significant impact, in particular in the Adige and Ebro: positive trends of water temperature and negative of dissolved oxygen are correlated with upward trends of air temperatures. The aquatic ecosystems of these rivers are, therefore, experiencing a reduction in oxygen, which may exacerbate in the future given the projected further increase in temperature. Furthermore, monthly streamflow has been shown to reduce in the Ebro, thereby reducing the beneficial effect of dilution, which appears evident from the observed upward patterns of chloride concentrations and electrical conductivity. Upward trends of chloride and biological oxygen demand in the Adige and Sava, and of phosphate in the Adige appears to be related to increasing human population density, whereas phosphates in the Sava and biological oxygen demand in the Ebro are highly correlated with agricultural land use, considered as a proxy of the impact of agricultural practises.

The present study shows the complex relationships between drivers and observed changes in water quality parameters. Such analysis can represent, complementary to a deep knowledge of the investigated systems, a reliable tool for decision makers in river basin planning by providing an overview of the potential impacts on the aquatic ecosystem of the three basins.

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1. Introduction

The ecological and chemical status of freshwater has attracted a wealth of attention in the last decades (e.g., Vega et al., 1998; Ahearn et al., 2005). Water bodies hosting important ecosystems are subjected to anthropogenic and climatic stressors often acting in synergy. To assess the effects of actions aimed at improving the ecological status of freshwater ecosystems, monitoring networks have been implemented in most of European basins, which provide a quite extensive database of water quality parameters (Benfenati et al., 2003). Despite this wealth of data, the connection between drivers and water quality parameters has not been fully exploited so far. Little is known beyond the effects of single stressors on the chemical and ecological status of water bodies and on their ecosystem functionality (Navarro-Ortega et al., 2015). This lack of knowledge limits our capability of understanding ecosystem responses to multiple stressors (Friberg, 2010), and as a consequence, the possibility for water and land use managers to determine suitable adaptive strategies for mitigating their effects. Many studies describe observed changes in chemical, ecological or hydrological variables (e.g., Bouza-Deaño et al., 2008), but few studies attempt to attribute causes of pattern variations (López-Moreno et al., 2011). Other works attempt to explain concentration patterns by using measurements of single sampling campaigns without considering long temporal variations (e.g., Kračun-Kolarević et al., 2016). Moreover, few studies assess long-term trends in water quality indicators at single gauging stations or detect alterations in the spatial patterns, chiefly because of data fragmentation and sampling discontinuity (Levi et al., 2015; Vrzel and Ogrinc, 2015).

The present work explores the complex interplay between water quality trends and the main drivers' observable at large scales and affecting surface water quality, by analysing whether observed changes are consistent with the drivers of change. To this aim, three large European river basins among the six included in the GLOBAQUA project (Navarro-Ortega et al., 2015) are studied: Adige, Ebro and Sava. The selection of these basins is made according to differences in hydro-climatic conditions and land use management, and to their contrasting resilience to climate change (Lutz et al., 2016). The main objectives of the present work are (i) to analyse long term water quality trends in each river basin, (ii) to identify links between observed patterns of physico-chemical variables and drivers (i.e., agriculture, streamflow, air temperature and population) in each basin, through quantitative analyses and (iii) to compare the studied basins with respect to their vulnerability and resilience to the identified drivers of change.

2. Study basins

The Adige River Basin is an alpine watershed located in the north-eastern part of Italy (Fig. 1A). With a size of about 12,100 km^2, it is the third largest Italian river basin. The large majority of the basin (91%) is Alpine and belongs to the Trentino Alto Adige region, while the remaining portion is the floodplain and is totally included in the Veneto region. The Adige River has a length of 409 km and drains into the Adriatic Sea (Chiogna et al., 2016). Its main tributaries are: Passirio, Isarco, Rienza, Noce, Avisio, Fersina and Leno. Streamflow shows a typical alpine regime with two maxima, one occurring in spring due to snowmelt and the other one in autumn triggered by cyclonic storms. In the alpine portion of the catchment, elevation ranges from 120 to 3400 m a.s.l. Climate is typically alpine with dry winters, snow and glacier-melt in spring, humid summers and autumns. The long-term annual mean temperature is 3 °C and annual average precipitation is 1456 mm (both evaluated in the time span 1961–1990; Lutz et al., 2016).

The Ebro River Basin is mainly located in the north-eastern part of Spain (Fig. 1B). With a catchment area of 85,362 km^2, the Ebro is the largest river basin of Spain. The basin extends from the Pyrenees and the Cantabrian Range in the north (maximum altitude of more than 3000 m a.s.l.) to the Iberian Range in the South and the Coastal Range in the East (López-Moreno et al., 2011). The Ebro River has a length of 910 km and it drains into the Mediterranean Sea with a mean

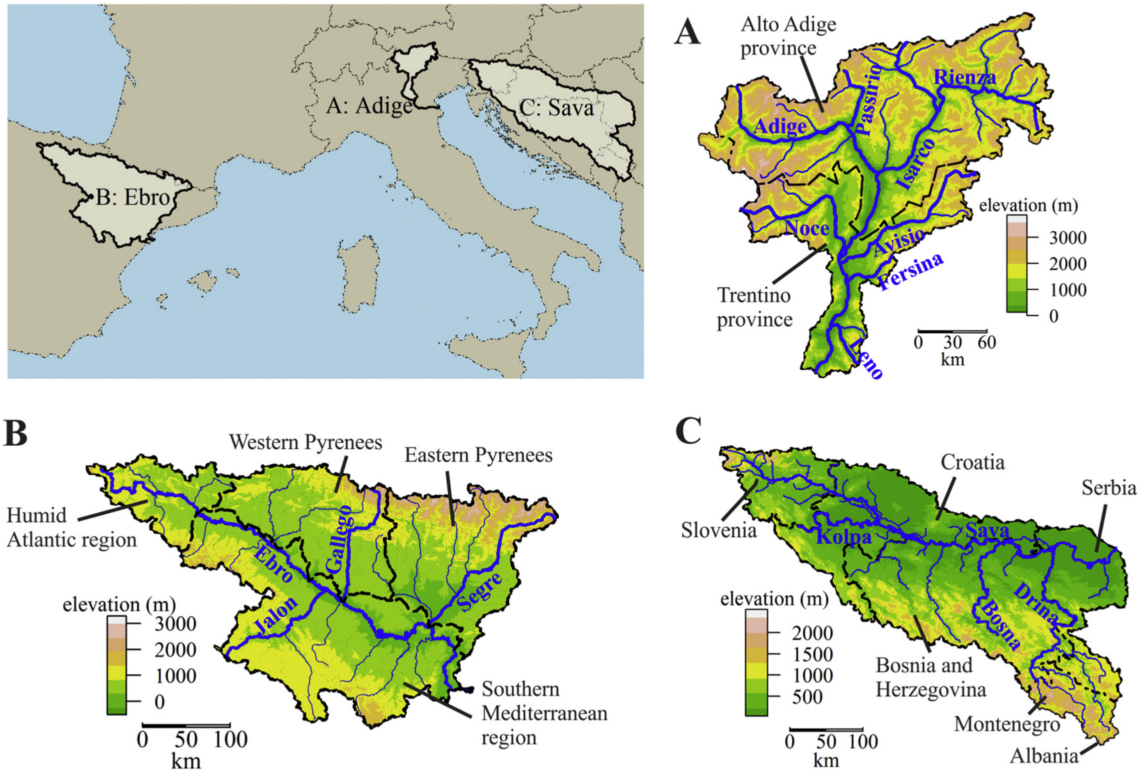


Fig. 1. Southern Europe map with the locations of the investigated river basins. Elevation maps and the river networks (up to the second order streams) are shown in sub-panels (A), (B) and (C) for the Adige, Ebro and Sava, respectively.

streamflow of 425 $m^3 s^{-1}$. Segre, Cinca, Aragón, Gallego, Jalon and Zadorra are the main tributaries of the Ebro River.

Long-term mean annual air temperature is 11.4 °C and mean annual precipitation is 620 mm (both evaluated in the time span 1920–2000; Sabater et al., 2009). The climate is mostly continental-Mediterranean, since it ranges from semi-arid in the centre of the river valley to oceanic in the Pyrenees and Iberian Mountains.

The Sava River Basin is located in the southern part of the Danube Basin (Fig. 1C) and drains into the Black Sea. With a catchment area of 97,713 km^2, the Sava is the second largest tributary of the Danube after the Tisza River. Altitude ranges from 71 m a.s.l. at the catchment outlet to 2778 m a.s.l. in the Slovenian alpine headwaters (ISRBC, 2013). The Sava is a transboundary river and its basin encompasses 6 countries: Slovenia (11% of the total catchment area), Croatia (26%), Bosnia and Herzegovina (40%), Serbia (15.4%), Montenegro (7.5%), and a minor portion in Albania (0.1%). It is 945 km long and it drains into the Danube in Belgrade (Serbia). Climatic conditions along the river course range from alpine to continental. Long term annual mean temperatures, evaluated between 1971 and 2000, range from 6 °C in the mountain regions to 13 °C close to the river mouth (Ogrinc et al., 2015). Mean annual precipitation, evaluated between 1961 and 1990, ranges from 800 mm to 1600 mm (Ogrinc et al., 2008).

3. Data and methods

For reasons of comparability between the three basins, the study period was set from 1990 to 2015: restriction to the time frame was necessary because of the limited availability of measurements for some variables in the Sava and Adige basins and the availability of Corine Land Cover information (EEA, 2013), which is available only since 1990. As suggested by Hirsch et al. (1991), only those stations with long records (i.e., at least 24 measurements during the study period) were considered in all the three basins to perform trend analyses. Data were organised into two groups: variables and drivers (for data sources and details, see Sections 3.2 and 3.3). The former included water quality data used to detect the trends, while the latter included selected important factors available continuously in time at the European scale, i.e., instantaneous and monthly aggregated streamflow, monthly aggregated air temperature, human population density and percentage of agricultural land use. The percentage of artificial areas such as “urban fabric”, “industrial, commercial and transport units”, “mine, dump and construction sites” and “artificial, non-agricultural vegetated areas” (cf. Corine Land Cover class information), was discarded from the analysis due to the similarity in the spatial patterns with population density. Hence, the driver population density was assumed as an indicator of the overall anthropogenic impact. Other determining features were not included in the statistical analyses because of the difficulty to obtain them at monthly time scale and for all the investigated catchments. These include treated and untreated waters, livestock density, industrial outflows, mining activities, crop choices, and intensity of agricultural production, which may be considered in future studies at smaller scales (e.g., specific regions of large river basins). Nevertheless, annual data of livestock and phosphate fertilisers for the three basins were used in order to support the discussion. Data were downloaded from the Italian institute of statistics (ISTAT, 2016) for the Adige basin and from the Food and Agriculture Organization of the United Nations (FAOSTAT, 2015) for the Ebro and Sava basins. In detail, for the Adige basin, information on phosphate fertilisers and livestock are available in the periods 2003–2015 and 2002–2016, respectively, but aggregated at regional scale, which is wider than the Adige catchment of about 3000 km^2. For the Ebro, the data refer to the whole area of Spain. Phosphate fertiliser data are available for the period 2002–2014 and livestock data for the period 1990–2014. Finally, for the Sava, data are aggregated at each national scale (i.e., Croatia, Serbia, Montenegro, Slovenia, and Bosnia and Herzegovina) over periods that vary depending on the country. For phosphate fertilisers, the longest period is 2002–2014, while for livestock density, the longest period is 1992–2011 only for Bosnia and Herzegovina, Croatia and Slovenia.

3.1. Statistical methods

Trends and drivers of change were analysed by applying the Spearman rank correlation, Principal Component Analysis, and Mann-Kendall trend test to the available time series. The Spearman rank correlation (Spearman, 1904) was calculated to preliminarily estimate the level of correlation between the physico-chemical parameters and drivers. Spearman's R is a special case of the Pearson coefficient in which the data are converted to ranks before calculating the correlation coefficient (Bouza-Deaño et al., 2008). The Spearman rank correlation was performed between all pairs of variables and drivers at each station for the three basins. Subsequently, mean R coefficients were calculated in order to identify correlations as general descriptors of the interplay between water quality parameters and drivers.

Principal Component Analysis (PCA) is a powerful technique of multivariate data analysis useful for identifying patterns in data (Wackernagel, 1995; Shrestha and Kazama, 2007). In the present work, PCA was applied separately to the complete dataset (both variables and drivers) of each study basin in order to screen temporal and spatial patterns and to select meaningful synthesis variables facilitating the ensuing analyses. PCA was also used to validate the results of Spearman rank correlation, with the further advantage of encompassing spatial information.

Since water quality data follow skewed distributions, trend analyses were performed with the nonparametric Mann-Kendall (MK) test in all river basins (Mann, 1945; Kendall, 1975). The MK-test does not require a priori assumptions of the underlying distributions and should be preferred to parametric trend tests in the analysis of multiple datasets (Hirsch et al., 1991). In order to calculate the sign and magnitude of trends, Sen's slope estimator was determined from the MK-statistics because it does not require the underlying probability distribution to be Gaussian and it is less sensitive to outliers than the Ordinary Least Square (Sen, 1968). The statistical significance of trends is defined using a significance level of $\alpha = 0.1$ for Kendall's p-value. MK trends and Sen's slope estimator were computed for time series of water quality variables with at least 24 measurements. All statistical and graphical analyses were performed using R statistical software packages (https://www.r-project.org).

3.2. Water quality variables

Physico-chemical variables were available at monthly resolution at 45, 42 and 22 monitoring stations in the Adige (Fig. 2A; http://www.appa.provincia.tn.it; http://www.provincia.bz.it/agenzia-ambiente/), Ebro (Fig. 2B; http://www.datossuperficiales.chebro.es:81/WCASF/) and Sava (Fig. 2C; http://www.icpdr.org/wq-db/), respectively. The dataset used in this work includes only variables, selected from larger sets of parameters, that are in common among the three basins: pH, water temperature (TW), electrical conductivity (cond) and concentrations of arsenic (As), biological oxygen demand (BOD5), chemical oxygen demand (COD), dissolved oxygen (DO), total nitrogen (N_{tot}), phosphates (PO_4), total phosphorus (P_{tot}), chloride (Cl), suspended solids (SS) and sulphates (SO_4). All variables are expressed in mg L^{-1} except pH [−], electrical conductivity [$\mu S\ cm^{-1}$] and water and air temperatures [°C]. Dissolved oxygen as % saturation was not included in the present analysis due to the lack of complete time series. Station locations and main statistics of the 13 variables are provided in the Supplementary material (SM). Concentrations below the detection limit were discarded prior to the analysis (Hirsch et al., 1991).

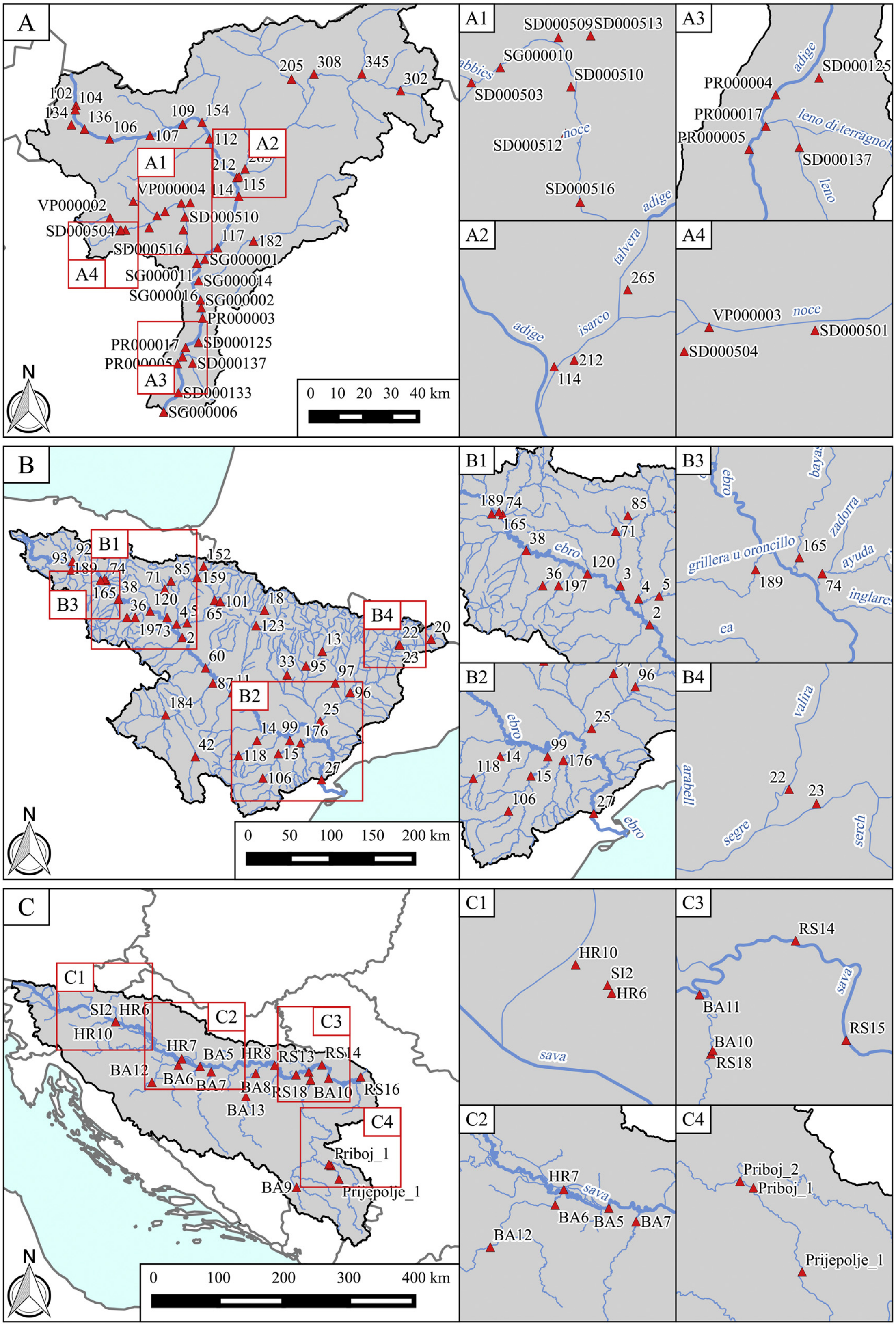


Fig. 2. Locations of water quality sampling stations for Adige (A), Ebro (B) and Sava (C), respectively. Identifiers refer to the original codes as retrieved from the case-specific water agencies. Right-side picture enlargements show regions with a high station density.

3.3. Water quality drivers

Sources of information for each river basin and gap filling procedure of instantaneous streamflow time series (Q) are provided in the SM. Coupled with Q time series, monthly aggregated data (Q_m) were also introduced as a proxy of the seasonality of the hydrological cycle. Monthly time series of air temperature (TA) were extracted from the version 12.0 of the 0.25° resolution E-OBS gridded dataset (Haylock et al., 2008) by selecting the temperature of the grid cells containing the sampling points. The dataset was downloaded from http://www.ecad.eu.

Percentage of agricultural land use retrieved from Corine Land Cover (years 1990, 2000, 2006 and 2012; EEA, 2013) is assumed as an indicator of the impact of agricultural activities, while population is considered as a proxy of urban areas and the associated contaminant loads. Although a more detailed small-scale analysis of industrial activities, including mine production and agriculture, may provide additional insights, available data currently do not allow this type of analysis.

Human population data at an interval of 5 years from 1990 to 2015 were obtained from NASA-Socioeconomic-Data-and-Applications-Center (CIESIN, 2017). For each river basin, drainage areas at the sample locations were determined from the European-wide digital elevation model provided by the GMES RDA project (EEA, 2017). Annual population and agriculture data were then aggregated at the level of the single sub-basin by linearly interpolating between the two closest years with information in the dataset.

4. Results

4.1. Trends in drivers

Preliminary analyses of the selected drivers were conducted in order to investigate their temporal and spatial patterns in the study period (Figs. 3, 4 and Table 1).

MK-trend analysis of Q_m time series in the period 1990–2015 evidences a predominance of negative trends for the three basins. The declining trend is stronger (i.e., larger absolute value) in the Adige (Fig. 3A), particularly in the Noce sub-catchment, than in the Ebro (Fig. 3C) and Sava (Fig. 3E). However, the southern part of the Ebro is instead characterized by the predominance of positive trends in the gauging stations.

For what concern temperature, Adige and Ebro show large positive MK trends in TA (Fig. 3B and D); this tendency is not confirmed in the Sava, where TA is nearly constant (Fig. 3F).

The percentage variations of agricultural land use and population density were derived for the three basins in the period 1990–2015. In the Adige, agricultural area decreased from 1990 to 2012 (−1.27%) while population increased (+17.81%). The reduction of agricultural area is most pronounced in the catchments of the tributaries Noce, Fersina and Avisio (Fig. 4A). Population increased over the majority of the sub-basins, with areas in the South and West showing the strongest population growth (Fig. 4B). In the Ebro, agricultural area decreased in the period 1990–2012 (−9.68%), particularly from 2006 to 2012, whereas population increased by more than half (+53.12%) between 1990 and 2015. The reduction of agricultural land use is strongest in two headwaters in the western and north-eastern portions of the basin, respectively (Fig. 4C). The latter region also shows the largest population growth. Population has reduced only in two headwaters of the southern Mediterranean region (Fig. 4D). In the Sava, agricultural area decreased slightly between 1990 and 2012 (−3.08%), while population remained fairly stable between 1990 and 2015. At the regional scale, agricultural land use shows a slightly to moderately reduction in all sub-basins except in the south-eastern region (Fig. 4E). Regarding population, the upper and middle sections of the main river have experienced little change; in particular the Drina sub-basin (i.e., the south-eastern region) shows a decreasing tendency similar to the middle section South of the Sava River, and the Bosna sub-basin (between the latter two areas) shows increasing population (Fig. 4F).

4.2. Correlation analysis

The statistical methods described in Section 3.1 were applied to the physico-chemical parameters and drivers. The Spearman's R rank correlation applied to the water quality indicators and drivers (Fig. 5) helps in

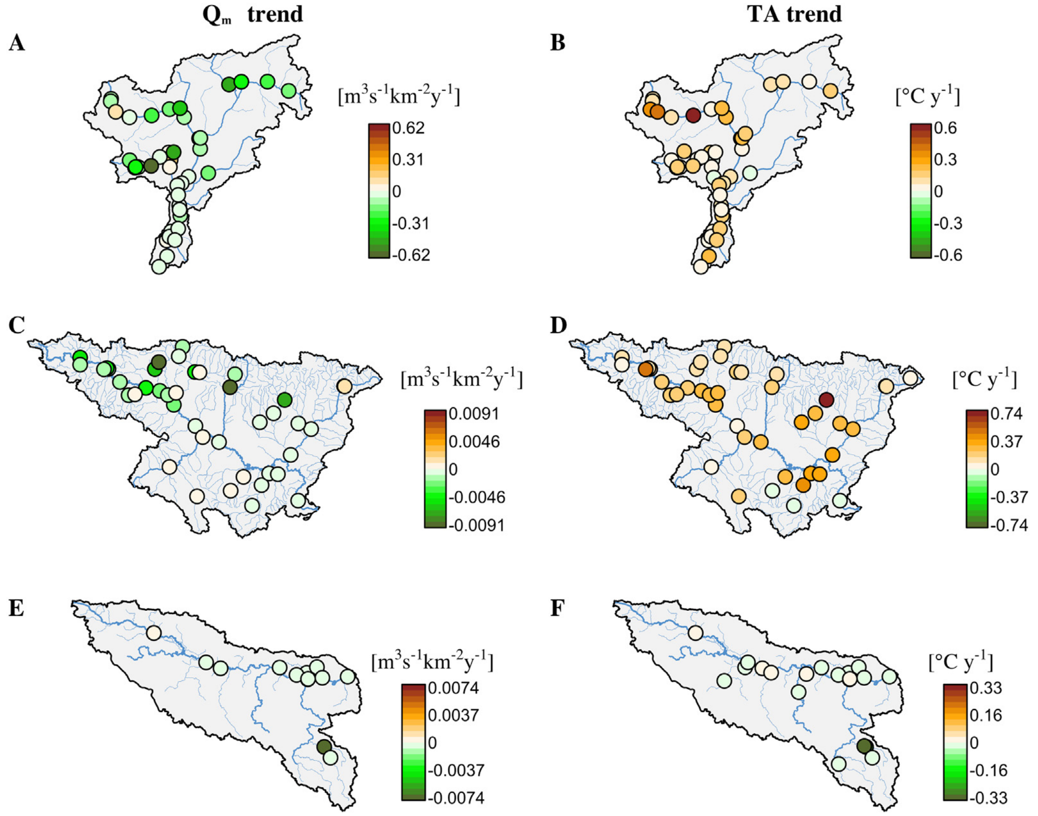


Fig. 3. Sen's slope trend magnitudes of monthly specific streamflow (left) and monthly air temperature (right) for Adige (A, B), Ebro (C, D) and Sava (E, F), respectively. Changes for both drivers refer to the period 1990–2015. In order to make the time series of the three basins comparable, streamflow time series were normalised by the drainage area at the sampling point.

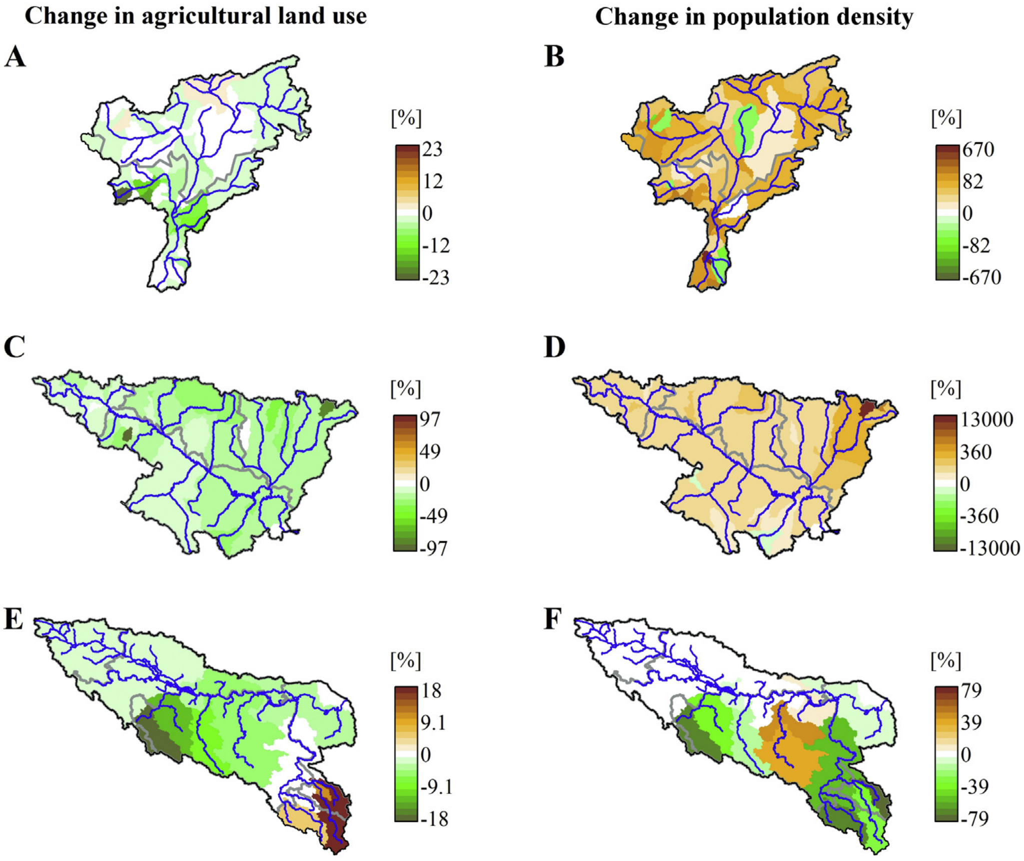


Fig. 4. Relative changes in the proportion of agricultural land use (left) and population per km^2 (right) aggregated over the sub-basins in the Adige (A, B), Ebro (C, D) and Sava (E, F). Changes in agricultural land use refer to the period 1990 to 2012 for the Adige (A) and Ebro (C), and to the period 2000 to 2012 for the Sava (E), respectively. Population changes are calculated for the period 1990 to 2015 in all basins.

selecting among the 13 physico-chemical variables those that better represent the geochemical behaviour of the catchment for the successive comparison with the drivers of change. Spearman's R rank coefficients indicate that the Adige basin has, in general, the highest mean correlations between the largest numbers of variables compared to Ebro and Sava. Electrical conductivity (cond), SO_4, Cl and DO are negatively correlated with TA, while SS and TW are positively correlated with Q and Q_m. Differences are observed in the behaviour of physico-chemical variables in the three river basins. For example, both in Ebro and Sava, concentrations of Cl and SO_4, electrical conductivity, and TW show positive correlations with TA, and all are negatively correlated with streamflow. On the other hand, similarities among the three basins emerge when considering negatively correlated pairs such as DO versus TA and TW and Q_m versus Cl. Similarly, positive correlations are observed in all basins between TW and TA, which is expected being air temperature an important determinant for water temperature. As expected, Q and Q_m show a similar degree of correlation with geochemical variables, with Q_m showing a slightly larger correlation compared to Q. On the contrary, agricultural land use and population are weakly correlated with geochemical variables. In particular, the Adige dataset shows the lowest correlations: only population shows a negative correlation with BOD5, N_{tot}, PO_4, and P_{tot}. The highest correlation with these drivers is observed in the Ebro for As concentration. Furthermore, moderate mean positive correlations between agriculture and N_{tot}, and between agriculture and PO_4, respectively, are observed in the Ebro and Sava.

Table 1
Percentages of agricultural land use and average population density for each basin in the study period according to data availability. The percentages of variation are calculated as the increase/decrease between the first and the last available dates. A) Percentages of agriculture among the whole basin area are provided in the years 1990, 2000, 2006 and 2012. B) Population density, referred to the whole area of each basin, is available every 5 years from 1990 to 2015.

		ADIGE	EBRO	SAVA
A				
Agriculture [%]	1990	14.64	48.05	43.17[a]
	2000	14.49	47.95	42.93
	2006	14.57	47.75	42.44
	2012	14.46	43.40	41.84
	% variation 1990–2012	−1.27	−9.68	−3.08
B				
Population [inhabitants km^{-2}]	1990	48.91	24.81	72.81
	1995	50.10	25.27	71.94
	2000	50.35	30.69	74.45
	2005	52.64	32.64	73.68
	2010	55.06	35.35	73.13
	2015	57.63	37.99	72.81
	% variation 1990–2015	+17.81	+53.12	0.00

[a] Land cover data not available for Bosnia and Herzegovina.

Spatio-temporal variations in driver-variable correlations might be masked because correlation coefficients at the sampling locations were averaged over the basin. To remove possible masking effects, PCA was performed. PCA is a robust technique for correlation analysis, which is not influenced by masking effects and eliminates accidental correlation (Fig. 6). The basin with the highest variance explained by the first two principal components is the Sava (46.6%), followed by Adige (45.6%) and Ebro (41.9%). The results for the Adige basin (Fig. 6A) confirm what was expected from geological characteristics; in the northern portion of the Adige (stations 104, 106, 107, 109, 136 – the location of these stations is shown in Fig. 2A), arsenic and sulphates are geogenic, since they are not correlated with anthropic factors such as agricultural land use and population. In the middle of the river basin

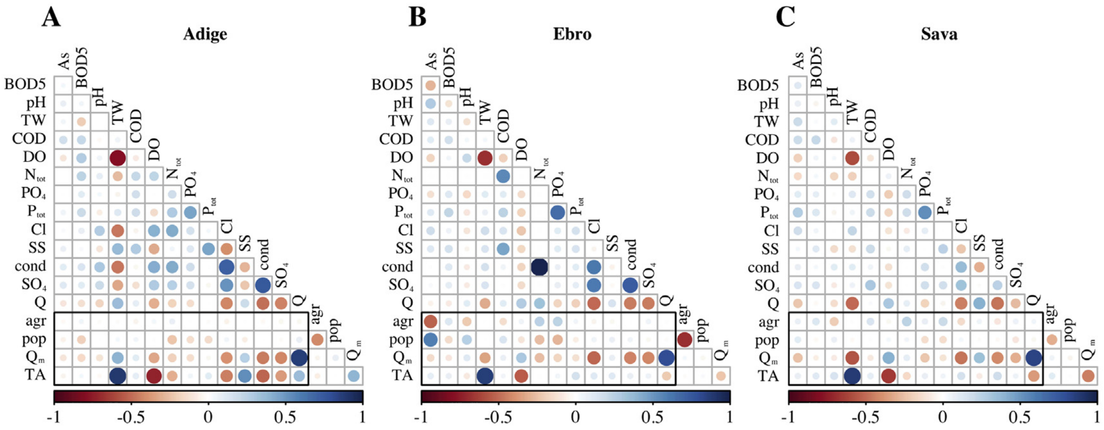


Fig. 5. Matrices of mean Spearman correlation between variables and drivers (black rectangles) for Adige (A), Ebro (B) and Sava (C) river basins obtained by averaging the correlation coefficients identified for each sampling location; red and blue dots correspond to negative and positive correlations, respectively. Small dots with light colour intensity represent low correlations while big dots with darker colours correspond to higher correlations. The rows in the correlation matrices referring to the drivers, which are agricultural land use (agr), population (pop), monthly mean water discharge (Q_m) and monthly mean temperature (TA), are included in a rectangular box. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(stations 115, 117, 212), at station SG000002 (Trento-Adige River) and at station 308 (Rienza River), anthropogenic influences are predominant: Cl, N_{tot}, pH are in fact correlated with agricultural land use and population. Moreover, PO_4 is highly correlated with streamflow. TA influences mostly stations 114, 265, 205 and shows positive correlations with TW, P_{tot}, BOD5 and SS, while it is negatively correlated with electrical conductivity and DO.

In the Ebro basin, stations 101, 106, 18, 96, 97, 36, 3 (Fig. 2B) are not influenced by any of the four drivers; however, pH and DO are the predominant variables for these sites: in fact, the respective arrows in Fig. 6B are oriented toward the projected observations of these stations. Conversely, stations 11 and 20 are much more influenced by anthropogenic factors such as agricultural land use and population; both are highly correlated with SS and less with streamflow. Electrical conductivity, Cl, PO_4, COD and BOD5 show high positive correlations with agricultural land use and they are predominant at the sites 60, 33, 38 and 74. Finally, TA is highly correlated with TW and As, the correlation is positive, and it influences stations 14, 15, 99 and 25. As opposed to the Adige, where stations can be divided into two groups according to PCA results, no clear drivers can be identified for the Ebro and the data do not show clustering effects.

Finally, in the Sava basin, most of the sampling sites are highly influenced by agriculture: agricultural land use shows large correlations with SS and N_{tot} (Fig. 6C). The only sampling site with a marked different behaviour is SI2 (Fig. 2C), where population is the most influential factor: in fact, the variable has a strong positive correlation with pH and, differently from the other sites, SI2 seems to be much more affected by anthropic activities.

In general, the analyses of the three basins confirm that DO is negatively correlated with TA whereas water and air temperature are highly correlated. These are expected results given that in surface waters air temperature is the main controlling factor of water temperature and oxygen saturation in water depends on the water temperature.

4.3. Trends in water quality variables

In the following, we consider only parameters showing the highest correlations with drivers and describe the type of anthropogenic impact associated with the driver according to previous research. Based on these criteria, BOD5 and PO_4 were further analysed because of their correlation with agricultural practises (e.g. Nash et al., 2015). Cl and electrical conductivity were considered because of their correlation with anthropogenic activities (e.g., contaminant releases from urban areas and mines), and industrial activities (e.g. Halstead et al., 2014). Electrical conductivity is also associated with variations in dissolved solids originating from land run-off (Chapman, 1996). In addition, DO concentration was selected as a primary physico-chemical variable for supporting interpretation of biological data (European Commission, 2009) given its importance for the aquatic life (Kannel et al., 2007). In fact, various aquatic species are particularly sensitive to changes of DO (see e.g., Kramer, 1987; Bierman et al., 1994; Caraco and Cole, 2002; Sánchez et al., 2007; Schmidtko et al., 2017). TW was selected because it influences the degradation of organic substances and is strongly correlated with TA, thereby encapsulating one of the most important effects of climate change in the riverine ecosystem (Gibson et al., 2005). Moreover, hereafter, we consider as driver only Q_m and no longer Q, as these two factors show very similar correlations with the drivers (see Figs. 5 and 6).

Trend detection is influenced by the length of the time series, because cyclic variations at scales larger than the time window are seen as a trend (Hirsch and Slack, 1984). To evaluate how large scale variations change with time, trend analysis was performed by using a moving time window of 10 years spanning the entire 1990–2015 time frame for six selected physico-chemical parameters (Fig. 7). Notice that oscillating trends obtained with a moving window of 10 years is indicative of variability with time scales of the order of 10 years, or less, while persistent trends are indicative of larger scales of variability.

DO shows a general negative trend with a small temporal variability in all decades and all basins: in both Adige and Ebro the majority of the stations show a downward trend, which intensified in the last decades (Fig. 7A). Cl, PO_4 and BOD5 (Fig. 7B, D, and E) show oscillating behaviours in the 90s, but a stable, yet small, trend in more recent years. Both Cl and BOD5 show increasing trends for Ebro in the same decades (2002–2011, 2003–2012 and 2004–2013). Electrical conductivity does not show significant trends in the Adige, whereas it oscillates in the Sava and, in particular, in the Ebro basin (Fig. 7F). The only basin showing increasing trends in electrical conductivity since 2003 on is the Sava. TW is the variable with the lowest variability, with a limited number of stations showing significant MK trends (Fig. 7C). However, present trends indicate an increase of TW in the Ebro and a reduction in the Sava, particularly in the decade 2006–2015.

Significant MK trends of a water quality parameter at a given station were associated with the drivers by using the Spearman rank correlation (Fig. 8). TW is the only variable with positive trends in all the basins, though in the Adige and Sava this trend is significant only at a few stations. PO_4 trends are all positive in the Adige (Fig. 8A) and related

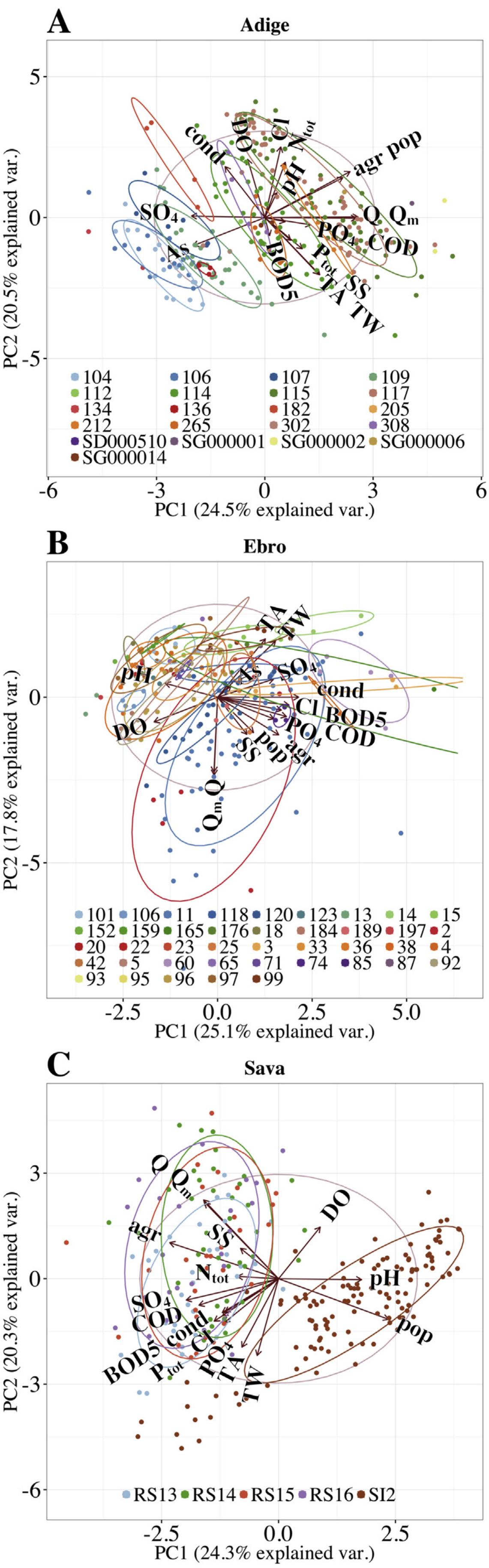


Fig. 6. Biplot representation of Principal Component Analysis between all-time series of Adige (A), Ebro (B) and Sava (C), respectively. Points represent observations projected in the new reference system (PC1–PC2) and a different colour is assigned to each sampling site. Ellipses represent normal data probability with a confidence interval of 68%. Arrows represent variables whose reliability, in terms of variance, in the dataset is explained by their length; the angle between two arrows corresponds to their mutual correlation: 90° represents absence of correlation, whereas angles less than 90° indicate increasing positive correlation, and angles larger than 90° indicate increasing negative correlation.

to three out of four drivers, while in the Ebro and Sava the simultaneous presence of both positive and negative trends is observed. Moreover, Sava (Fig. 8C) shows the largest percentage of positive trends for Cl and BOD5, while Ebro presents the largest percentage of negative trends for DO. Percentages of significant positive and negative trends, associated with each driver, with respect to the total number of sampling stations in each basin, are provided in Table 5S of the SM.

In the Adige, TA is the main driver of change for DO. Positive and negative trends are balanced with the latter dominating the north-western portion of the basin (Fig. 8A). Cl concentrations show positive trends controlled predominantly by population in the north-western portion and by both population and the hydrological driver (Q_m) along the main stem after the confluence of the Isarco river (see Figs. 1A and 8A). Positive trends in PO_4 and BOD5 are instead associated with population, though at a few stations it is the hydrological driver that exerts the main influence on the trend. Electrical conductivity and TW show significant trends in a small percentage of stations without a dominant driver. Note that in the north-eastern portion of the basin only a very limited number of monitoring stations show trends in the water quality variables.

In the Ebro, trends of DO are predominantly negative and associated with TA, though at some stations the negative trend is associated with streamflow, which is also the main driver of change for chloride and electrical conductivity. Agricultural land use is the main driver of change for BOD5, and population for PO_4. Overall, trends are predominantly negative for DO and positive for PO_4 and electrical conductivity, whereas for the other parameters positive and negative trends are balanced and without evident spatial patterns (see Fig. 8B and Table 5S in the SM).

In the Sava, less significant trends are observed, but they are still appreciable. Chloride is correlated with all the drivers except population, showing predominantly negative trends and no evident spatial patterns (Fig. 8C). PO_4, BOD5 and electrical conductivity show positive trends correlated with agricultural land use, with BOD5 related to population. Finally, TW shows a single positive trend associated with the hydrological driver.

5. Discussion

DO is one of the most commonly used parameters for assessing ecosystem conditions, and it also influences solubility of potentially harmful metals (Chapman, 1996). It is inversely proportional to TW and hence TA, as confirmed in all the three basins by rank correlations (Fig. 5), PCA (Fig. 6) and trend analyses (Figs. 7 and 8). The significant correlation of DO with TW was expected according to Henry's fundamental physical law (Henry, 1803) and thus it confirms that the dataset is of adequate quality to identify trends. Such correlation has been widely observed in the literature (see e.g., Chapra, 2008; Villeneuve et al., 2006), In fact, Figs. 3 and 8 show downward DO patterns in the north-western part of the Adige River, which is associated with upward trends of TA (Fig. 3B). Similar considerations are applicable to the north-western part of the Ebro basin (Fig. 3D) and to the eastern part of the Sava (Fig. 3F). Even though TA is evidently the main driver of DO in all basins, DO concentrations were also observed to correlate with streamflow (Fig. 8). In fact, DO concentrations are usually lower when streamflow is low (e.g. Balls et al., 1996; Cox and Whitehead, 2009; Zhang et al., 2016): this is observed in the western part of Ebro and

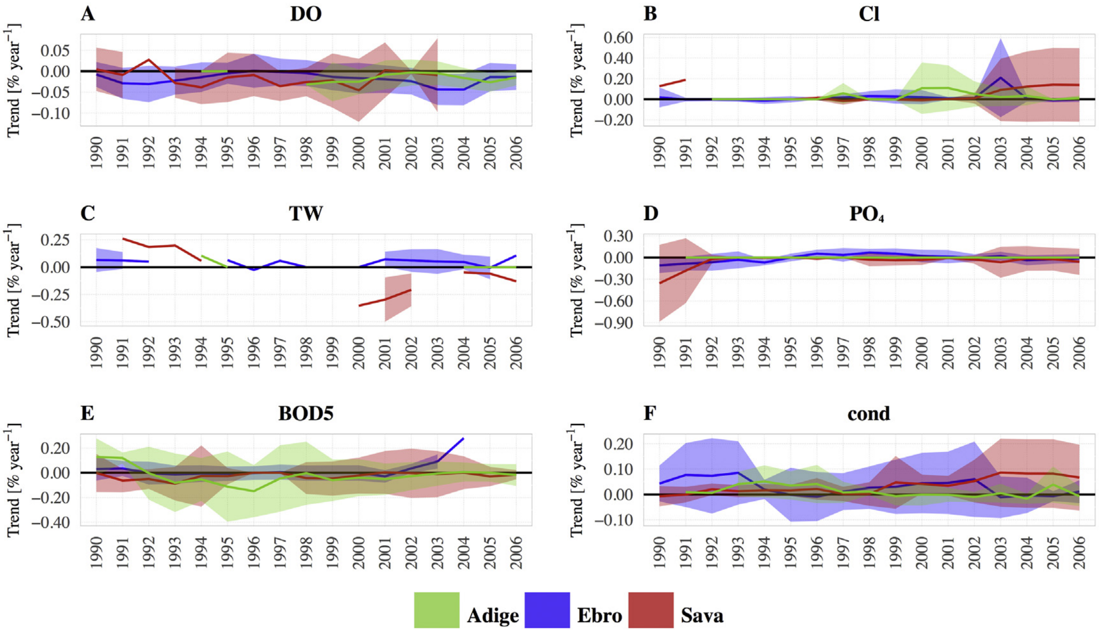
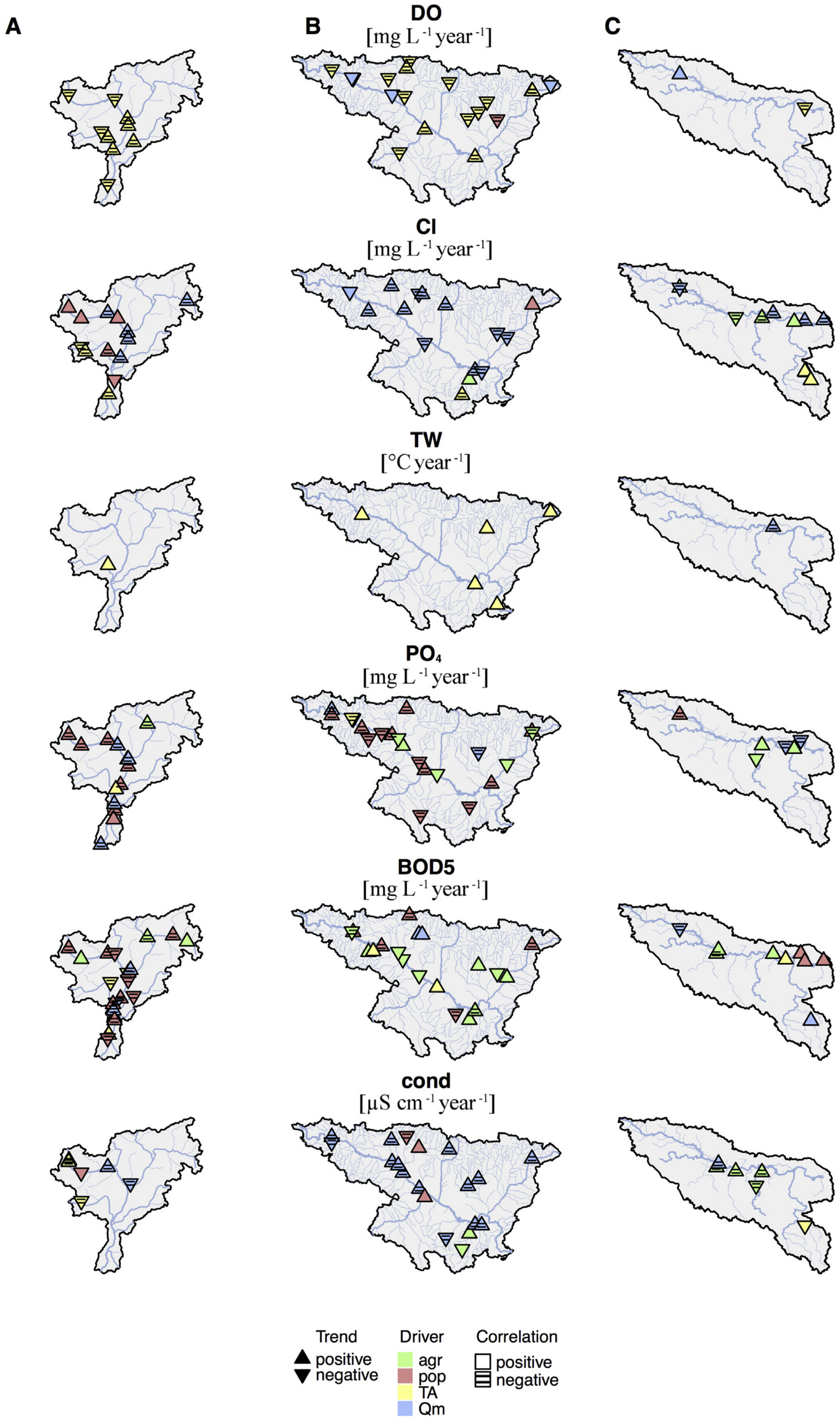


Fig. 7. MK mean trends (expressed as annual percentages of variation with respect to mean concentrations) on a moving time window of 10 years in the period 1990–2015 for the 6 water quality variables averaged over all the water quality stations of each basin. The abscissa shows the initial time of the 10 years window; therefore, the trend associated to the year 1990 is computed over the time window 1990–1999, and the trends for the following years up to 2006 are determined accordingly. Thick lines represent the mean trend whereas light colours indicate uncertainty bands expressed by standard deviation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Sava basins (Fig. 3C–E), but not in the Adige where DO correlates negatively with Q_m (Fig. 5A). The latter evidence is probably due to the typical alpine hydrological regime of the Adige basin, with high streamflow occurring in summer. This suggests, in line with the findings of Cox and Whitehead (2009) for the Thames River and highlighted for the present study by Figs. 5 and 8, that temperature is an important driver for DO even more than streamflow. In the Sava basin, DO trends are positive where streamflow increases and negative where TA increases; however, according to this study, changes are relatively small.

Another important factor affecting DO is the concentration of nutrients, which is provided both by nutrient-rich agriculture return flows (Jalali and Kolahchi, 2009) and by organic loads, the latter in the case of a concurrent alteration of electrical conductivity (Daniel et al., 2002; Ortiz et al., 2005; Calapez et al., 2017). In fact, nutrients promote biological activity, creating dead and decaying biomass which consumes DO as respiration (Odum, 1956; Null et al., 2017). Moreover, the amplitudes of daily oxygen level variations were found to be strongly correlated with average nitrate concentration (Villeneuve et al., 2006). In the present study, though nutrients are not the primary drivers of DO changes, DO and phosphates are negatively correlated, especially in the Ebro and Sava basins, whereas the Adige basin is much less affected by nutrients (Fig. 5). In addition, the Ebro and Sava basins are characterized by inverse correlations between DO and electrical conductivity, suggesting an influence of organic loads by wastewater on the observed DO decrease. Comparing the three basins, Ebro shows the greatest number of DO downward trends (Table 5S in the SM) and, moreover, downward patterns are mostly associated with upward trends of TA. The combined effects of reduction of DO and streamflow (Lutz et al., 2016), the latter being associated with reduction of precipitations and increase of TA, suggests that the Ebro is the basin with potentially the highest alterations of chemical and biological processes due to climate change (Aguilera et al., 2015; Bouza-Deaño et al., 2008).

High chloride concentrations in surface waters may negatively impact aquatic life (Nielsen et al., 2003). Sources of chloride in surface waters are atmospheric deposition, weathering of sedimentary rocks, sewage and industrial effluents, agricultural and road run-off (Chapman, 1996). Dilution is crucial in limiting chloride concentrations in all the three basins, as chloride is negatively correlated with streamflow (Fig. 5). As chloride concentrations in the Ebro are governed by the geology of the drainage area (Bouza-Deaño et al., 2008), positive Cl trends in the Ebro basin are likely due to the reduction of streamflow (Figs. 7 and 8B). An evident increasing trend in Cl concentrations is in fact observed in the north-western portion of the Ebro basin, where the reduction of streamflow is pronounced (Fig. 3C). A possible mechanism behind the increasing trend in Cl concentration is the increase of residence time, due to the reduction of streamflow, and therefore enhanced rock weathering, while the decrease of dilution due to streamflow reduction from areas not releasing Cl may have a synergetic effect. Similar behaviours are observed in the central area of the Adige and in the eastern portion of the Sava basin, albeit Cl is also correlated with population in the Adige and with agricultural land use in the Sava (Fig. 8). In this context, population can be considered as a proxy of the impact of urban areas: in fact, municipal sewage treatment plants use chloride for removal of suspended particles and bacteria and to enhance the removal of phosphorus (Rogora et al., 2015). Nevertheless, road salt may also be a relevant source of these ions to surface waters, particularly in mountain catchments, where urban or industrial releases are expected to be of minor importance (Rogora et al., 2015). The combined analysis of Figs. 4B and 8A leads to the conclusion that upward patterns of Cl in the north-western portion of the Adige basin and in the Noce sub-basin are linked to anthropogenic pressure. In the Sava, although analyses evidenced a predominant correlation with agriculture, the concurrent effect of anthropogenic emission of chloride has to be considered. In fact, the Sava River Basin is a very complex system influenced by industry, mining, treated and untreated wastewaters (Drolc and Končan, 1996; Dragun et al., 2009; Milačič et al., 2010; Heath et al., 2010). Untreated urban wastewaters are of particular importance in Bosnia and Herzegovina and Serbia in the South-East of the basin, where less than 10% of agglomerations with a person equivalent of above 2000 apply some kind of wastewater treatment (ISRBC, 2016). In addition, the major sources of surface water pollution in the southern part are industrial activities, farms and settlements which discharge untreated waters (Pivic et al., 2014). Moreover, the presence of salt mines in Bosnia and Herzegovina (Mancini et al., 2009) increased Cl


A
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BOD5
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cond
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Trend
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negative
Driver
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TA
Qm
Correlation
positive
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concentrations in Bosna River, one of the main tributary of the Sava River. This is exacerbated by changes in the hydrogeological conditions, which enable the downward flow of freshwater causing additional salt dissolution (Mancini et al., 2009). Hence, the significant positive trends of Cl in the southern part of the Sava basin (Fig. 8C) might be mainly related to industrial and mining activity (Markovics et al., 2010).

TW does not show a clear pattern in all basins, which is due to the filtering effect (i.e., removal of stations presenting non-significant trends) of the Mann–Kendall test. Nevertheless, only positive trends are detected (Fig. 8), which are linked to TA in Adige and Ebro, and to monthly streamflow in the Sava. This may evidence that climatic conditions (i.e., increasing TA) are impacting rivers by increasing TW. In fact, a larger TW leads to larger reaction rates of chemicals, which helps in degrading reactive contaminants, but at the same time causes alterations in the biogeochemical conditions (Gibson et al., 2005).

Phosphorus is generally the limiting nutrient for algae growth (Chapman, 1996). Increases in phosphorus concentrations may be both of natural and anthropogenic origin: weathering of rocks containing phosphorus, decomposition of organic matter, fertiliser run-off and releases from domestic or industrial wastewater treatment plants (WWTPs) are the possible sources. Unlike previous variables, phosphate is less influenced by streamflow (Fig. 8). Trends in the Adige basin are only positive in the period 1990–2015 and, according to our analyses, they are mainly correlated with population. This suggests that the principal source of phosphorus in the basin is anthropogenic, as also confirmed by Benfenati et al. (1992). Even though 80% P-removal at wastewater treatment plants outflows in rivers is required in Italy according to national law (D. Lgs n. 152, 11/05/99), an increase in population may have attenuated the positive effects related to the implementation of this policy. Consequently, the increase of population in the southern and western areas of the basin (Fig. 4B) may drive a further increase in phosphate concentrations. Unfortunately, information and studies on river nutrient loads, and in particular phosphates, are still incomplete for the Adige, as also suggested by Cozzi and Giani (2011). Phosphate fertilisers and livestock data (ISTAT, 2016) are available for the period 2002–2015, at annual scale and aggregated for the whole Trentino Alto Adige region, thus referring to an area larger than the Adige basin of about 3000 km^2. These data did not show significant variations in the use of phosphate fertilisers, even if annual oscillations are quite pronounced (ranging from 8 to 65 kg km^{-2} in 2013 and 2014 respectively). Indeed, the number of adult bovine animals is slightly decreasing, with a peak of 20 units km^{-2} in 2012 and a minimum of about 12 units km^{-2} in 2014. These considerations reveal that increasing phosphate concentrations in the Adige basin can hardly be attributed to agriculture and livestock farming.

Similar correlations are observed in the Ebro basin, where the positive trends in PO_4 correlate the most with population. This is consistent with Torrecilla et al. (2005) and Aguilera et al. (2015), who emphasize the important role of point sources, such as urban and industrial areas, in controlling phosphate concentration in rivers. In addition, livestock density increased in Spain, from a minimum of 17 units km^{-2} in 1990 to a maximum of 24 units km^{-2} in 2007 (FAOSTAT, 2015). It is worth noticing that these data refer to the entire state. However, downward patterns are also observed in some areas of the Ebro basin (Figs. 7 and 8), possibly associated with the reduction in the use of fertilisers. Notice that in Spain the use of fertilisers declined from 1200 to 700 kg km^{-2} in the period 2002–2014 (FAOSTAT, 2015), as a positive effect of the introduction of drip irrigation (Bouza-Deaño et al., 2008) and improvements in sewage treatment (Aguilera et al., 2015). Given the overall downward trend in the proportion of agricultural land use (Fig. 4C), the downward trend in the phosphate input from fertilisers might be counterbalanced, in the future, by the need to sustain the growth of specific and more water-use efficient productivity (Graveline et al., 2014). In the Sava, trends are on average upward but, in contrast to the Ebro, the largest number of positive trends is linked to agriculture. One possible source may be the use of P-containing fertilisers in rural areas of Croatia, Bosnia and Herzegovina and Serbia (Milačič et al., 2010; Pivic et al., 2014), also according to the FAOSTAT (2015) data, which showed positive trends in the use of phosphate fertilisers in these three countries. Hence, our analysis identifies in agriculture a significant source of phosphate, supplementing and in some cases overcoming the release from urban settlement, indicated as the main factor by Vrzel and Ogrinc (2015). This implies that phosphate concentrations might increase in the south-eastern region of the Sava, where agriculture expanded in recent years (Fig. 4E). Moreover, livestock density increased across the basin, especially in Slovenia where it reached the highest values of the whole basin in 2011 with 103 units km^{-2} of cattle (FAOSTAT, 2015). Hence, this might also lead to increasing phosphate concentrations in the upstream section of the river basin. Nevertheless, the use of P-containing detergents released by municipal sewages and untreated waters might be important additional sources of phosphorus mainly in the northern part of the basin (Milačič et al., 2010).

BOD5 is a measure of the amount of biochemically degradable organic matter contained in the water (Chapman, 1996): high concentrations of BOD5 in rivers produce, in general, oxygen depletion due to the decay of organic compounds (Sincock et al., 2003). The main sources of degradable organic matter are urban areas, but it may also originate from run-off of agricultural areas and cattle (Fernández-Alvarez et al., 1991). In all the three basins, we observed a prevalence of significant positive trends in BOD5, whose sources are mainly urban for Adige and Sava and agricultural for the Ebro (Fig. 8). Consequently, pollution with organic compounds may increase with population, particularly in the south of the Adige basin (Fig. 4B), and in parts of the middle portion of the Sava basin (i.e., Bosnia and Herzegovina; Fig. 4F), respectively. For the Adige basin, the introduction of the 70–90% BOD5-removal at WWTPs outflows (D. Lgs n. 152, 11/05/99) seems insufficient to counterbalance the increase of population. For the Ebro, in contrast, concentrations of organic compounds might decrease given the downward trend in the proportion of agricultural land use (Fig. 4C). However, this might not apply to organic pollutants that are mainly discharged in industrial and municipal wastewater (e.g., alkylphenols; Terrado et al., 2010). In general, BOD5 is expected to be inversely proportional to Q_m because of dilution (Lehmann and Rode, 2001); however, both correlation and PCA analyses highlight a poor correlation between BOD5 and Q_m in all basins (Figs. 5 and 6). BOD5 best correlates with agriculture and population but not with streamflow (Fig. 8): this highlights the influence of anthropogenic activities on BOD5, as also confirmed by previous studies in the Adige (Benfenati et al., 1992), Ebro (Bouza-Deaño et al., 2008) and Sava (Paunovic et al., 2008).

Correlation between electrical conductivity and urban development is reported and such dependence has been attributed to the wash-off of solutes from hard surfaces in urban areas (Prowse, 1987; Chapman, 1996). In the Adige, electrical conductivity can be considered stable given the limited number of identified trends (both positive and negative). This contrasts with the Ebro and Sava, where significant and spatially coherent trends have been observed (Fig. 8). In the Ebro, the predominance of positive trends is mainly associated with the reduction of streamflow; while in the Sava the positive trend is associated with

Fig. 8. Significant MK trends over the period 1990–2015 for the stations of Adige (A), Ebro (B) and Sava (C) river basins, respectively. Direction of triangles expresses the Sen's slope trend sign, whereas colours represent the driver with the maximum absolute value of Spearman correlation with the water quality parameter. Lines inside each triangle indicate a negative correlation between variables and the respective drivers; the absence of lines indicates positive correlations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

agricultural activity (Figs. 4E and 8), though a previous work indicates an industrial source of electrical conductivity (Dragun et al., 2009). In addition, electrical conductivity is sensitive to variations in dissolved solids originating from land run-off (Chapman, 1996). However, it was not possible to analyse this factor in detail given the large-scale scope of this study.

6. Conclusions

This study compares trends in water quality parameters of three large European river basins, characterized by different hydroclimatic and socio-economical conditions, and attempts to link them to the main drivers of change. The principal results of this study can be summarised as follows:

(i) Agriculture has been proved to affect BOD5, in particular for the Ebro, where the amount of organics in freshwaters is linked to the trends in the proportion of agricultural land use. Moreover, positive trends in PO_4 in the Sava are shown to be affected by increasing agricultural land use and thus likely by an increased use of fertilisers; instead, in the Ebro, downward trends may be explained by the reported reduced use of fertilisers and improvements in sewage treatment. It was additionally shown that agricultural practises also affect Cl and electrical conductivity in the Sava, whose positive trends are probably due to the increase of agricultural activities and hence land run-off.

(ii) Population affects Cl in the Adige, where the recent increase in resident population, in particular in the north-western areas, has enhanced Cl emissions related to industrial activities, urban releases and use of road salt in winter. Additionally, BOD5 patterns in the Adige and Sava are shown to be correlated with population. Trends of PO_4 are, on average, positive for the Adige and are found to be correlated with population increase and thus with intensification of human activities.

(iii) The reduction of the dilution effect, mainly due to decreasing streamflow, is particularly evident in the Ebro and explains positive trends of Cl and electrical conductivity. Moreover, as expected, observed trends in DO are linked to both hydroclimatic drivers (i.e., Q_m and TA). Since DO is the variable presenting the largest number of negative trends in all the basins, an increasing risk of low DO is highlighted and it may have adverse effects on aquatic ecosystems, in particular in the Ebro, where downward DO trends are widespread and persistent.

(iv) TA, being a proxy of changing climate, is undoubtedly an important driver that influences mostly TW and DO. Due to the limited data availability and the absence of significant MK trends, only few positive trends in TW have been observed. However, increases in TA are found to be correlated with observed upward patterns of TW.

(v) The present work highlights the complex relationships between sources of pollution and water quality parameters, and demonstrates the importance of well-equipped and carefully managed monitoring networks. Complementary to a deep understanding of the local system, statistical data analyses can represent a reliable tool for decision makers in river basin planning by providing them with an overview of the potential impact of ongoing climatic changes and river management policies on the aquatic ecosystem under investigation. We limited our analyses to few fundamental factors for which data are routinely monitored at the European scale, in order to implement statistical tools for data analyses. However, as there are numerous sources of water pollution, future studies might evaluate those at local scale and consider other compounds as indicators for diffuse pollution. In addition to data collection and analyses, local emission models might be beneficial for a complete understanding of water pollution at river basin scale.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.08.172.

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