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**Long-term dynamics of annual and seasonal physical and biogeochemical properties: role of minor river discharges in the North-western Adriatic coast; Estuarine, Coastal and Shelf Science; DOI: 10.1016/j.ecss.2022.107902**

To link to this article: <https://doi.org/10.1016/j.ecss.2022.107902>

This study has received funding from the EU Interreg Italy-Croatia WATERCARE Project 2019 (Water management solutions for reducing microbial environment impact in coastal areas - Grant 10044130); from University of Urbino, and Regione Marche Project of coastal monitoring n. 49 of December 23, 2013 (Table C).

## **Long-term dynamics of annual and seasonal physical and biogeochemical properties: role of minor river discharges in the North-western Adriatic coast**

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### **HIGHLIGHTS**

- Data series allowed assessing changing biogeochemical coastal dynamics.
- Role of the minor river inputs on interannual and seasonal biogeochemical dynamics.
- Oligotrophic trends in NW Adriatic coastal waters by reduced P and N riverine inputs.
- Nutrient load and climate changes as drivers of biogeochemical dynamics in Adriatic Sea.

### **Abstract**

Dynamics of the physical and biogeochemical properties in a temperate coastal area in the north-western Adriatic Sea were analysed. Multi-year (1997-2019) continuous observations allowed assessing their trends at two sites directly influenced by the discharges of two minor rivers as well as by human activities and climate change. Statistical models were applied to investigate the temporal variability and trends of seawater temperature, salinity, chlorophyll *a*, nutrients, river discharges and precipitations. The analysis highlighted a role for the minor river inputs and for ecological processes on interannual and seasonal biogeochemical dynamics. We found a significant trend toward more oligotrophic conditions; in particular, chlorophyll *a* exhibited a long-term decline ( $-1.38\% \text{ year}^{-1}$  and  $-1.5\% \text{ year}^{-1}$  at the two Foglia and Metauro river transects, respectively) that was largely determined by low phosphate and nitrate seawater concentrations as a result of a significant reduction in the phosphate and nitrate loadings of the two minor rivers (respectively mean values of  $-4.65\% \text{ year}^{-1}$  and  $-2.65\% \text{ year}^{-1}$ ). In contrast, salinity showed a long-term decrease of  $-0.24\% \text{ year}^{-1}$  and  $-0.19\% \text{ year}^{-1}$  at Foglia and Metauro, respectively, corresponding to a significant increase of the freshwater discharges of the two minor rivers ( $+1.86\%$  and  $+1.57\% \text{ year}^{-1}$  at Foglia and Metauro, respectively) possibly due to precipitations. Data analysis highlighted the conditions of temperate coastal areas affected by freshwater discharges. Nutrient load management and climate conditions such as precipitation regimes appear to be the main factors driving physical and biogeochemical dynamics in the north-western Adriatic Sea.

**Key words:** chlorophyll *a*; coastal zone; long-term series; northern Adriatic Sea; nutrients; run-off.

## 1. Introduction

In the Mediterranean Sea, the quality of marine ecosystems is being impacted by anthropogenic activities and climate change. The urbanization of coastal areas and estuarine areas, domestic and industrial wastewater discharges as well as economic activities such as fishery, aquaculture, and tourism, all exert a strong pressure on ecosystems (Micheli et al., 2013; Drius et al., 2019). These impacts are exacerbated by higher air maximum temperatures, by drought conditions, floods, and by high riverine inputs carrying nutrients and pollutants such as chemicals, plastic, and litter (Malone et al., 2014).

The Adriatic Sea is a basin of the Mediterranean Sea. In the north-western Adriatic Sea, which is characterized by shallow waters with low bathymetry. Ecosystem productivity in coastal areas is strongly linked to nutrient and organic matter discharges, carried by rivers from inland, besides basin and local circulation dynamics. Nitrogen and phosphorus have a predominantly anthropogenic origin, the former mainly from agriculture and livestock waste and the latter from urban and industrial wastewater (Grizzetti and Bouraoui, 2006; Viaroli et al., 2018). Thus, the biogeochemical and ecological processes of the coastal ecosystems in the North-western Adriatic Sea (Sverdrup, 1953) are affected by the prevalence of coastal inputs and lateral transport on water column processes, while shallow bottoms involve distinctive biogeochemical dynamics and processes that depend on site characteristics (Zavatarelli et al., 1998; Tedesco et al., 2007).

In the northern Adriatic Sea, the Po River is the main freshwater input source, contributing to about 50% of the total external nutrient input (Raicich, 1996; Campanelli et al., 2011). Its mean annual discharges of 1500-1700 m<sup>3</sup> s<sup>-1</sup> affects the northern Adriatic water circulation regime and trophic status (Fonda Umani, 1996; Artegiani et al., 1997; Degobbis et al., 2000), setting it apart from the Mediterranean basin, which is oligotrophic. The western Adriatic coast is characterized by low salinity and high nutrient content in proximity of the coast, and an oligotrophic regime offshore (Djakovac et al., 2012; Giani et al., 2012; Grilli et al., 2020). The

North Adriatic system is influenced by water circulation and water column stratification. In a mixing regime, the waters are transported southward by the Western Adriatic Current (WAC), whereas in stratified conditions the plume stays along the coast and spreads eastward (Marini et al., 2002; Grilli et al., 2005; Cozzi and Giani, 2011).

Since the 1970s, the northern Adriatic Sea has been subject to particularly intense eutrophication events, determined by excessive nutrient loadings due to algal blooms, which have degraded water quality, benthic habitats, and community structures (Provini et al., 1992; Rabalais et al., 2009; Howarth et al., 2011). The eutrophication has eventually been attenuated by improved environmental practices (Volf et al., 2018). In particular, EU directives regulating nitrate discharges (91/676/EEC) and urban wastewater treatment plants (91/271/EEC) have reduced nitrogen and phosphorus loads in river basins, although the measures aimed at controlling and reducing farming and livestock waste seem to have been less effective on nitrogen loads (Palmeri et al., 2005; Viaroli et al., 2018). However, nutrient loadings and the resulting eutrophication differ among regional watersheds and coastal areas in relation to land use, its evolution over time, in situ biogeochemical processes, marine currents, water column dynamics and, notably, climatic conditions, which affect river runoff to the sea (Romero et al., 2013).

The contribution of minor rivers to the trophic status of the Adriatic Sea has been the subject of several studies, which have examined freshwater discharges and nutrient loads (Campanelli et al., 2004; Marini et al., 2010; Cozzi et al., 2012; Giani et al., 2012). In the past few decades, river loads – also as a result of changed climate conditions and anthropogenic pressures – have often been the major allochthonous source of freshwater and nutrients, affecting coastal productivity, especially in the north-eastern Adriatic (Cozzi et al., 2020).

In 2000-2009, the eutrophication process in the north-western Adriatic was reversed by a combination of factors that included nutrient load mitigation strategies, a different land use of

watersheds, and reduced runoff due to drought (Mozetič et al., 2010; Djakovac et al., 2012; Maric et al., 2012). Indeed, in the past two decades, lower nitrogen, silicate, organic carbon, and total suspended matter transport, coupled with reduced total and inorganic phosphorus, have led to a shift to oligotrophic conditions (Degobbis et al., 2005; Cozzi et al., 2020). Further changes have been determined by a different land use of rivers and watersheds, while the climate is increasingly characterized by drought alternating with short but intense rain events (Ranzi et al., 2017). In addition, changes in agricultural and livestock activities and in urban land use, which in summer becomes more intense due to tourism, have contributed to reduce freshwater runoff to the sea (Viaroli et al., 2018).

In the present study, we present the first long-term analysis (1997-2019) of north-western Adriatic coastal waters in relation to the interannual and seasonal variation of biogeochemical properties, nutrient loadings, precipitation, and minor river discharges. The aim of this study was to test the hypothesis is that minor river discharges and climate change affect the biogeochemical dynamics of coastal waters in the north-western Adriatic Sea.

## **2. Material and Methods**

### *2.1 Study area*

The sampling area was in the north-western Adriatic Sea. This coastal zone is affected by Po River discharges, whose plume extends in N-S direction, and by the discharges of some minor rivers, chiefly the Foglia and the Metauro (actual mean discharges, 6.5 and 14 m<sup>3</sup> s<sup>-1</sup>, respectively). Water was sampled 0 m (at the river mouth), 500 m, and 3000 m from the coast, as follows: i) Foglia (43.925° N, 12.900° E), F500 (43.929° N, 12.900° E), and F3000 (43.952° N, 12.896° E), maximum depth 2.4, 6.5, and 13 m, respectively; and ii) Metauro (43.834° N, 13.055° E), M500 (43.837° N, 13.062° E) and M3000 (43.851° N, 13.077° E), maximum depth 3.5, 7.2, and 12.5 m, respectively (Fig. 1) (see also Ricci et al., 2014; 2016).

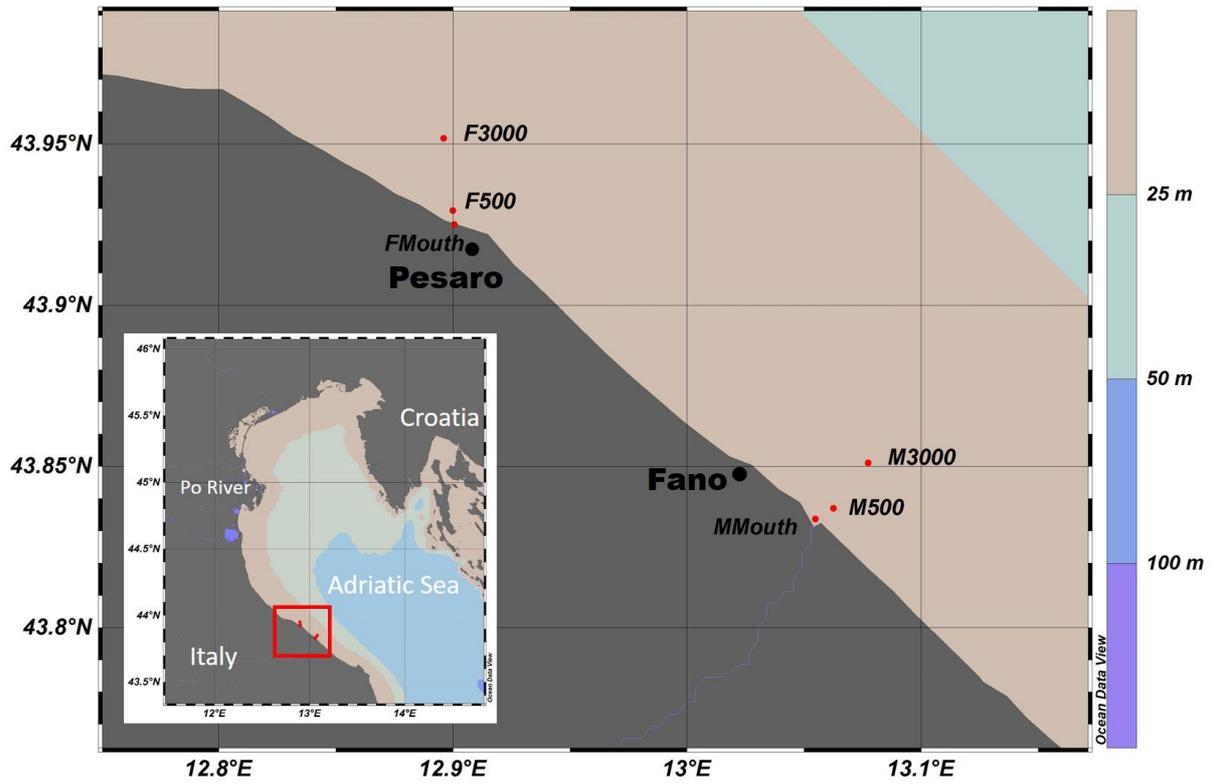


Fig. 1. Sampling stations in the North-western Adriatic Sea. The stations were located along two transects, respectively in front of the Foglia (F) and the Metauro (M) rivers, at 0 m (river mouth), 500 m (F500, M500) and 3000 m (F3000, M3000) from the coast.

## 2.2. Environmental data collection

The data were collected monthly at the 6 sampling stations over 23 years, from January 1997 to December 2019, and subdivided into seasons (spring, summer, autumn and winter) according to Artegiani et al. (1997).

Seawater temperature (°C) and salinity were measured with a CTD probe (Ocean Seven 316, Idronaut). Water samples for chlorophyll (Chl *a*) and nutrient (NO<sub>3</sub>, PO<sub>4</sub> and SiO<sub>2</sub>) analyses were collected using Niskin bottle and they were frozen at -20 °C, after filtration onto 0.45 µm nitrocellulose filters (Millipore, USA), until analysis.

The daily average flow rates (m<sup>3</sup> s<sup>-1</sup>) of the two rivers were estimated from the monthly average flow rates (m<sup>3</sup> month<sup>-1</sup>) published in the Annual Hydrological Reports-Part II and the Meteorological-Hydrological Information System of the Marche Region (both available at [www.regione.marche.it/Regione-Utile/Protezione-Civile](http://www.regione.marche.it/Regione-Utile/Protezione-Civile)). The hydrometric stations were located about 300 m (43.9076°N, 12.8977 E) and 100 m (43.8263 N, 13.0538 E) from the Foglia and Metauro mouths, respectively. As regards the unpublished data, the Foglia and Metauro flow rates were calculated from the hydrometric level through a rating curve. The daily precipitation data, published in the Annual Hydrological Reports-Part I, was recorded by pluviometric stations situated near the hydrometric stations.

## 2.3. Chlorophyll *a* and nutrient analyses

Chl *a* was determined in 90% acetone homogenates of particulate matter collected on nitrocellulose filters as described by APHA, AWWA, and WPCF (1985).

Dissolved inorganic nutrients were determined in filtered water samples by standard colorimetric methods with the azo dye test for NO<sub>3</sub> (detection limit > 0.1 µM) and the molybdate test for PO<sub>4</sub> and SiO<sub>2</sub> (detection limits > 0.03 and > 1 µM, respectively) using a UV-1700 Shimadzu spectrophotometer (Strickland and Parsons, 1972).

#### 2.4. Nutrient load analysis

The monthly  $\text{NO}_3$ ,  $\text{PO}_4$  and  $\text{SiO}_2$  discharge (F) was estimated by assuming a linear relationship between their concentrations and water flow (in tons month<sup>-1</sup>) as follows:

$$F \text{ (ton month}^{-1}\text{)} = C_i \cdot Q_{\text{month}} \cdot mA \cdot 10^{-6}$$

where  $C_i$  is the nutrient concentration (mol m<sup>-3</sup>) on each sampling day,  $Q_{\text{month}}$  is the cumulated monthly runoff (m<sup>3</sup> month<sup>-1</sup>) from the conversion factor  $2.5 \cdot 10^6$  (m<sup>3</sup> s<sup>-1</sup>),  $mA$  is the atomic mass of the biogenic element, and  $10^{-6}$  is the conversion factor (ton g<sup>-1</sup>).

#### 2.5. Time series analysis

Generalized linear model (GLM) regression along with *Gamma* as statistical distribution and “log” as link function was applied to estimate the time series. The model was fitted by adding first order interactions whenever it resulted in a better model (high proportion of deviance explained). GLM regression uses the method of least squares, linking the binary response to the explanatory covariates through the probability of either outcome. The transformed probability is then modeled with an ordinary polynomial function, linear in the explanatory variables (Ter Berg, 1980; Fokianos and Kedem, 2003). The *p*-values of the resulting Wald Chi-square tests were related to a significance value of  $p < 0.05$ . Seasonal long-term river flow trends and differences in flow amount between the Foglia and the Metauro were computed by non-parametric Spearman’s correlation and two-tailed Mann-Whitney U tests, respectively. The analyses were performed with PAST ver. 4.01 (Hammer et al., 2001). Data values are expressed with standard error (SE). The analysis of the trends was completed with that of the discontinuities in the series of the mean annual water discharge using SRSD method (Sequential Regime Shift Detector) (Rodionov, 2015). It is a parametric method based on

sequential t-test analysis used to identify regime shifts for the Foglia and Metauro discharges in this study.

### 3. Results

#### 3.1. Annual and seasonal trends of the physical, and chemical variables and chlorophyll a

The aggregated and seasonal data series (1997-2019) is reported in Suppl. Table 1. The biogeochemical properties of the Foglia and the Metauro showed no significant spatial differences ( $p < 0.05$ ) (Suppl. Table 2). The water temperature trends were not significantly different at the two sites, either according to the aggregated (Fig. 2a) or to the seasonal data (Figs. 3a and 4a). Surface salinity exhibited a significant downward temporal trend at both transects, both in the aggregated ( $-0.24\% \text{ year}^{-1}$  and  $-0.19\% \text{ year}^{-1}$  for Foglia and Metauro, respectively) (Fig. 2b) and in the seasonal data, particularly in winter, spring, and autumn (Figs. 3b and 4b).

Chl *a* showed a declining trend in the aggregated data ( $-1.38\% \text{ year}^{-1}$  and  $-1.5\% \text{ year}^{-1}$  for Foglia and Metauro, respectively) throughout the period at each river transects (Fig. 2c). The seasonal data demonstrated a similar significant reduction in winter and summer and a significant increase in spring at both sites. In autumn the trend was not significant (Figs. 3c and 4c). Nitrate showed a significant decreasing trend both in the aggregated and the seasonal data (Figs. 2d, 3d, and 4d) in all seasons with exception of summer without significant difference at both sites. Phosphate also exhibited a significant downward trend at both sites in both the aggregated and the seasonal data (Figs. 2e, 3e, and 4e). The silicate temporal trend was not significant either in the aggregated (Fig. 2f) or in the seasonal data (Figs. 3f and 4f).

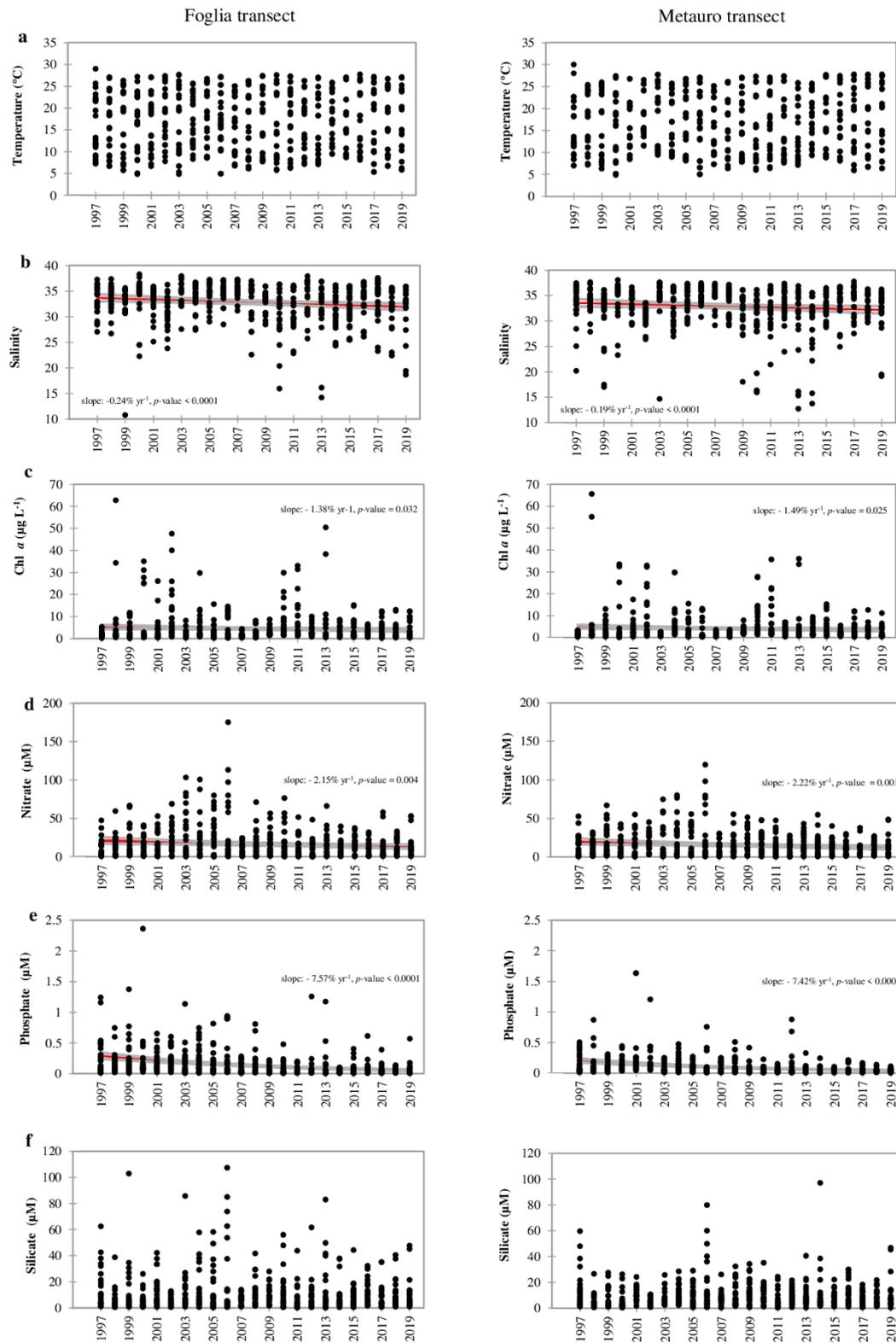


Fig. 2. Aggregated data trends of surface a) temperature ( $^{\circ}\text{C}$ ), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) and f) silicate ( $\mu\text{M}$ ) at the Foglia and Metauro transects in 1997-2019. Red line: long-term trend with 95% confidence limits that were shown by gray lines. The slope represents the annual increase or decrease percentage per each variable. The long-term regression is not reported when the slope was not significant ( $p > 0.05$ ).

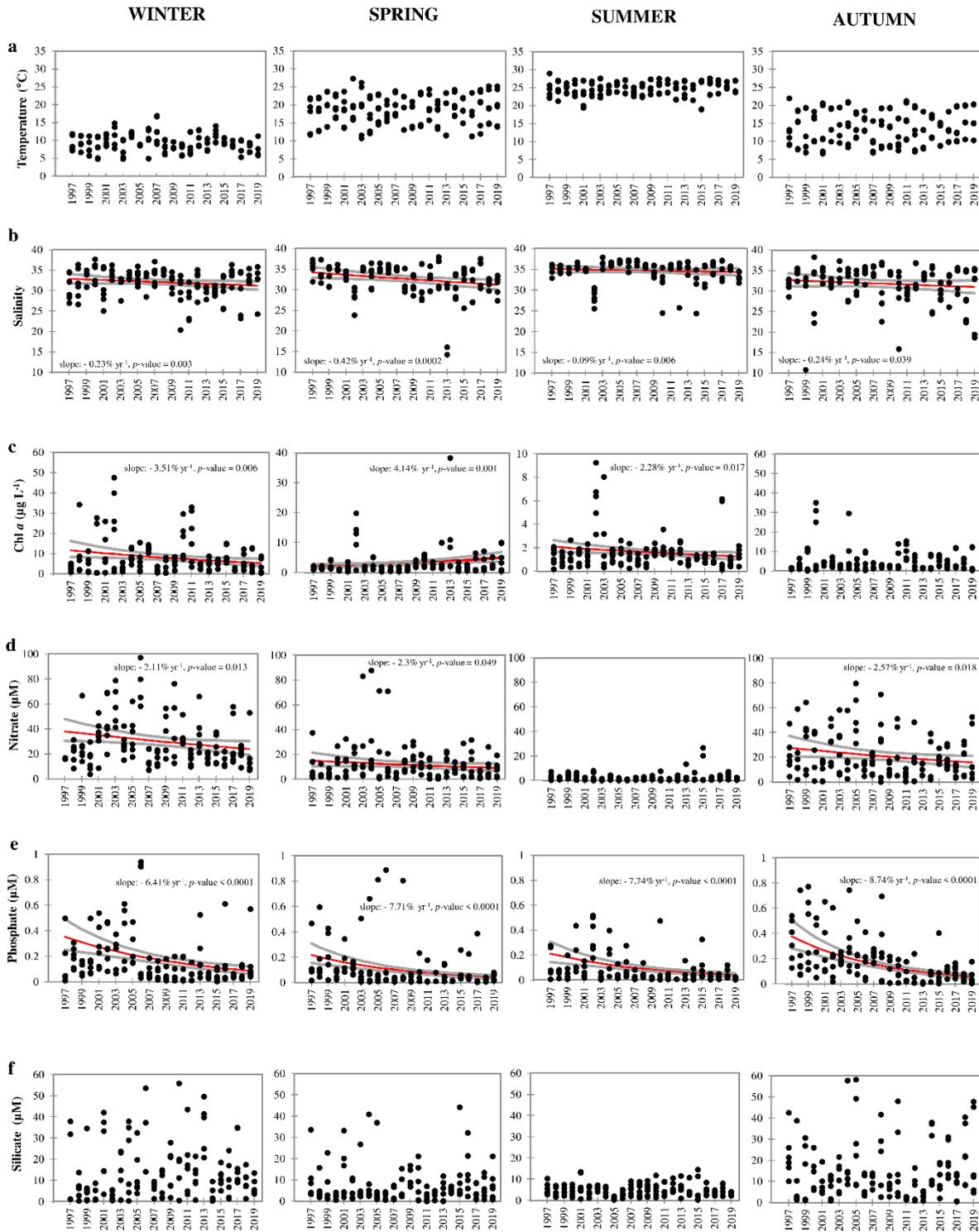


Fig. 3. Seasonal trends of surface a) temperature ( $^{\circ}\text{C}$ ), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) and f) silicate ( $\mu\text{M}$ ) at Foglia transect in 1997-2019. Red line: long-term trend with 95% confidence limits that were shown by gray lines. The slope represents the annual increase or decrease percentage per each variable. The long-term regression is not reported when the slope was not significant ( $p > 0.05$ ).

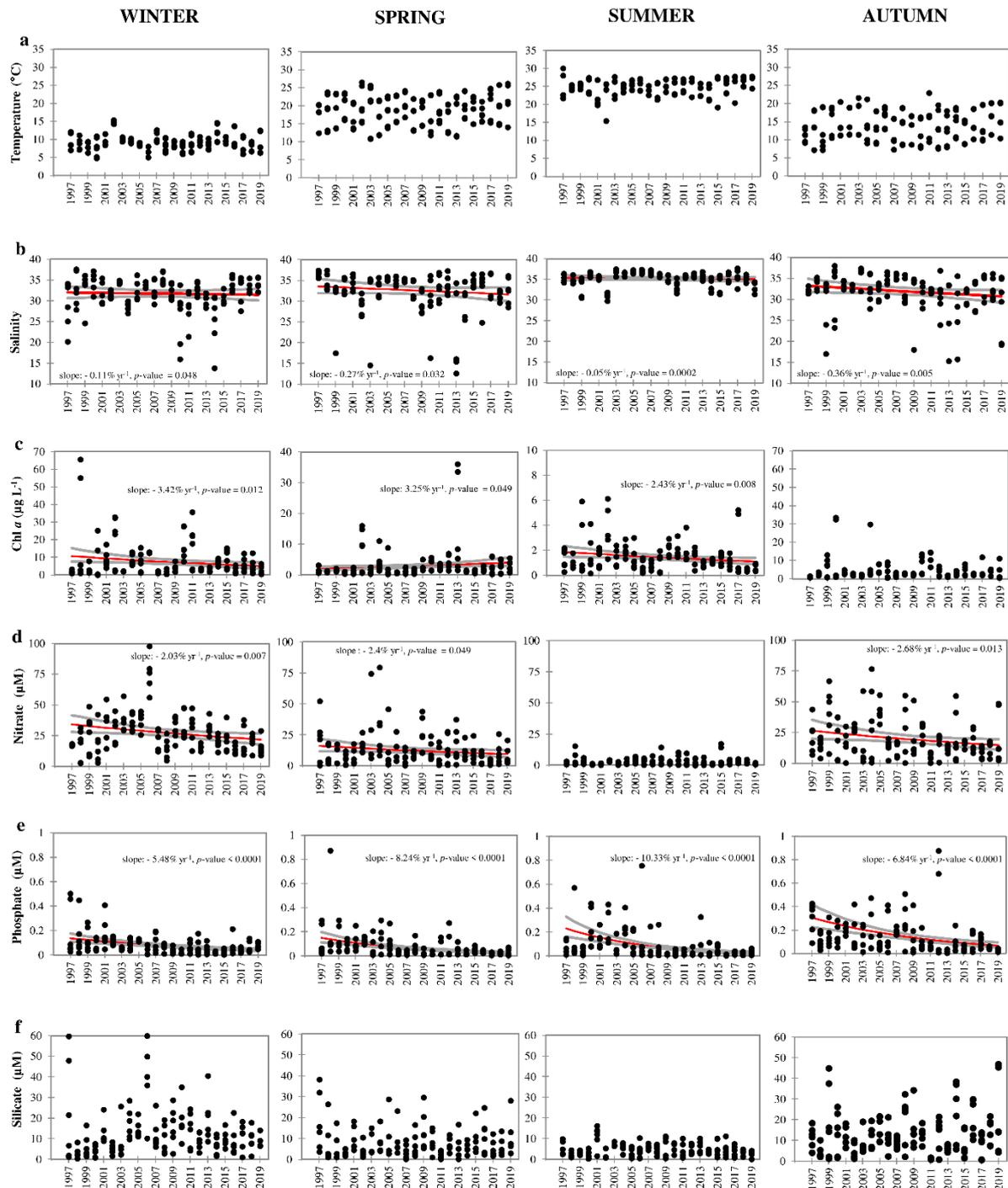


Fig. 4. Seasonal trends of surface a) temperature (°C), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) f) silicate ( $\mu\text{M}$ ) at the Metauro transect in 1997–2019. Red line: long-term trend with 95% confidence limits that were shown by gray lines. The slope represents the annual increase or decrease percentage per each variable. The long-term regression is not reported when the slope was not significant ( $p > 0.05$ ).

### 3.2. Annual cycle of physical and chemical variables, and chlorophyll *a*

Seawater temperature at the Foglia and Metauro transects showed a distinct seasonal cycle (Figs. 5a and 6a), with maximum in August (mean, 26.2 °C and 26.5 °C, respectively) and minimum in January (mean, 7.7 °C and 8.1 °C, respectively). The salinity seasonal cycle showed a variable pattern, with minimum in December (mean, 30.5 and 30.3, respectively) and maximum in August (mean, 35.2 and 35.4, respectively) (Figs. 5b and 6b).

Surface Chl *a* at the Foglia and Metauro transects showed a seasonal pattern characterized by some variability. Maximum was recorded in January (mean, 11.1  $\mu\text{g L}^{-1}$ ; range, 1.1 - 62.8  $\mu\text{g L}^{-1}$  and 10  $\mu\text{g L}^{-1}$ ; range, 0.9 - 65.7  $\mu\text{g L}^{-1}$ , respectively); however, an episodic biomass bloom in January 1998 reached values as high as 62.8 and 65.7  $\mu\text{g L}^{-1}$ , respectively. Minimum was consistently recorded in July (mean, 1.2  $\mu\text{g L}^{-1}$  at both sites) (Figs. 5c and 6c).

At both transects, nitrate and silicate exhibited a similar seasonal evolution with higher values in autumn-winter and lower values in spring-summer. Phosphate, which in the northern Adriatic Sea is the limiting nutrient, showed a high variability without a clear seasonal pattern and low concentrations (range, 0.01 - 2.3  $\mu\text{M}$ ) (Figs. 5d, e, f and 6d, e, f). In particular, the annual cycle of surface nitrate and silicate was characterized by maximum in February (mean, 35.2 and 30.2  $\mu\text{M}$  for N-NO<sub>3</sub>, at the Foglia and Metauro sites, respectively) and January (mean, 19.2 and 12.8  $\mu\text{M}$  for Si-SiO<sub>4</sub> at the Foglia and Metauro stations, respectively), with secondary maximum in December (mean, 32.8 and 29.7  $\mu\text{M}$  for N-NO<sub>3</sub>, and 22.5 and 18.1  $\mu\text{M}$  for Si-SiO<sub>4</sub> at the Foglia and Metauro transects, respectively). Minimum was recorded in July (2.65  $\mu\text{M}$ , Metauro) and August (1.38  $\mu\text{M}$ , Foglia) for N-NO<sub>3</sub>, and in July (4 and 5  $\mu\text{M}$  for Si-SiO<sub>4</sub> at the Foglia and Metauro sites, respectively).

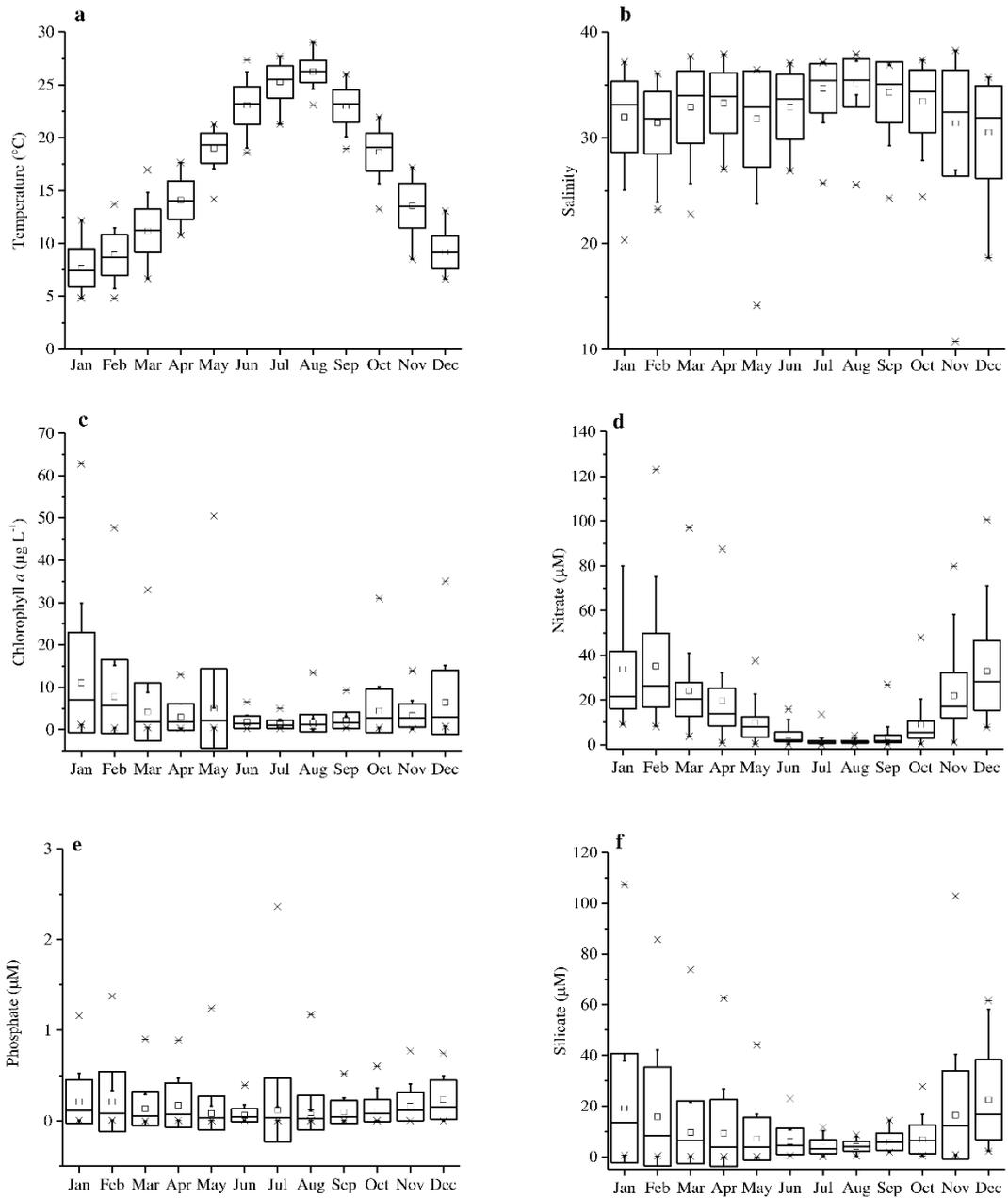


Fig. 5. Mean annual cycle of surface a) temperature ( $^{\circ}\text{C}$ ), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) and f) silicate ( $\mu\text{M}$ ) at the Foglia transect in 1997-2019. The box plots show the data distribution with mean ( $\square$ ), median (-), interquartile range (box), non-outlier range (vertical bars) and outliers (\*).

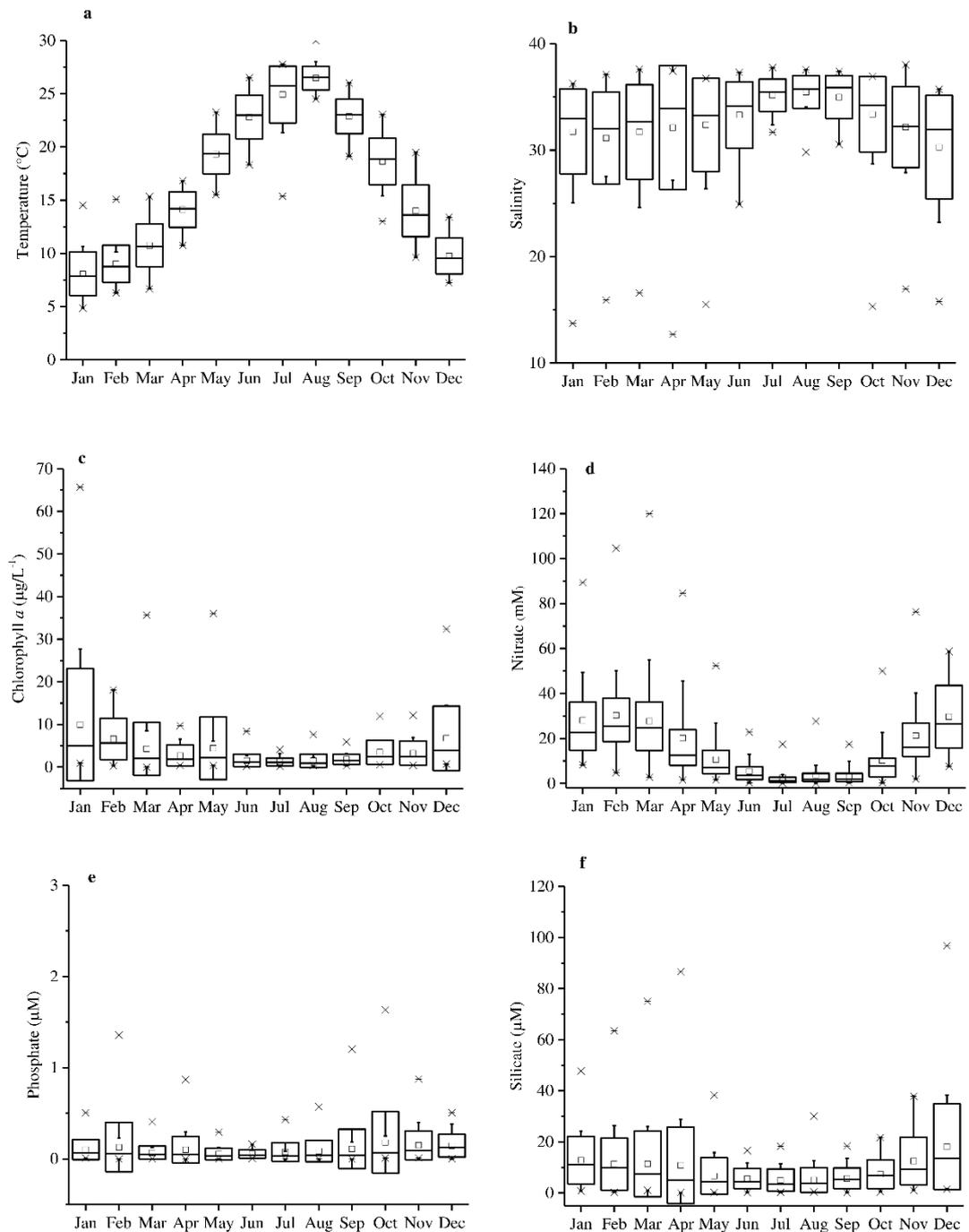


Fig. 6. Mean annual cycle of surface a) temperature ( $^{\circ}\text{C}$ ), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) and f) silicate ( $\mu\text{M}$ ) at the Metauro transect in 1997-2019. The box plots show the data distribution with mean (□), median (-), interquartile range (box), non-outlier range (vertical bars) and outliers (\*).

### 3.3. River discharges and precipitations

Data analysis highlighted significant differences in daily flow rates between the Foglia and the Metauro (Mann Whitney,  $p < 0.001$ ), with mean values of  $6.48 \pm 0.07$  and  $13.73 \pm 0.15 \text{ m}^3 \text{ s}^{-1}$ , respectively and ranges of  $0.1 - 232$  and  $0.1 - 344 \text{ m}^3 \text{ s}^{-1}$ , respectively (data not reported). The daily flow rates of both rivers showed a significant upward trend in the aggregated data ( $+1.86\% \text{ year}^{-1}$  and  $+1.57\% \text{ year}^{-1}$ ) (Table 1). As regards the seasonal flow rates, their trends were similar (Spearman, winter  $r_s = 0.673$ , spring  $r_s = 0.459$ , summer  $r_s = 0.178$ , autumn  $r_s = 0.561$ ,  $p < 0.05$ ) with a significant increase (expressed as annual percent variation) in winter ( $+5.59\% \text{ year}^{-1}$  and  $+4.01\% \text{ year}^{-1}$  for the Foglia and Metauro, respectively) and spring ( $+1.35\% \text{ year}^{-1}$  and  $+2.44\% \text{ year}^{-1}$ , respectively) and a significant reduction in summer ( $-2.69\% \text{ year}^{-1}$  and  $-1.24\% \text{ year}^{-1}$ , respectively) and autumn ( $-0.9\% \text{ year}^{-1}$  and  $-1.26\% \text{ year}^{-1}$ , respectively).

**Table 1.** Variation (% year<sup>-1</sup>) of daily Foglia and Metauro river flow ( $\text{m}^3 \text{ s}^{-1}$ ) and rainy day precipitation ( $\text{mm day}^{-1}$ ) at Foglia and Metauro meteorological stations in 1997-2019. Data was provided by Marche Region and Servizio of Protezione Civile. Data were estimated by Generalized Linear Model (GLM) regression. ns: not significant ( $p > 0.05$ ).

Parameter	Variation (% year <sup>-1</sup> )				
	Aggregated data	Winter	Spring	Summer	Autumn
Foglia river flow ( $\text{m}^3 \text{ s}^{-1}$ )	+1.86	+5.59	+1.35	-2.69	-0.90
Foglia precipitation ( $\text{mm day}^{-1}$ )	n.s.	+4.45	+2.44	-2.09	-4.30
Metauro river flow ( $\text{m}^3 \text{ s}^{-1}$ )	+1.57	+4.01	+2.44	-1.24	-1.26
Metauro precipitation ( $\text{mm day}^{-1}$ )	+0.95	+5.14	+2.41	-2.01	-1.49

The discharges of both rivers showed interannual variability (Suppl. Fig. 1). The multidecadal variations of the mean annual flow rate exhibited higher values in 2013 and 2014 for the Foglia (annual mean maximum,  $12.38 \text{ m}^3 \text{ s}^{-1}$  in 2013) and in 2013, 2014, and 2015 for the Metauro (annual mean maximum,  $20 \text{ m}^3 \text{ s}^{-1}$  in 2014). The Foglia flow was lower in 2006, 2007 and 2008 with annual mean minimum of  $2.47 \text{ m}^3 \text{ s}^{-1}$  with the lowest discharge registered in 2007 ( $2.3 \text{ m}^3 \text{ s}^{-1}$ , the lowest value). The Metauro discharges were lower in 2007, 2008 and 2009 with the lowest discharge registered always in 2007 (annual mean minimum  $6.0 \text{ m}^3 \text{ s}^{-1}$ ). The worst drought year was 2007 for both rivers. Further, a significant decreasing shift ( $-1.8 \text{ m}^3 \text{ s}^{-1}$  and  $-2.7 \text{ m}^3 \text{ s}^{-1}$  at Foglia and Metauro, respectively,  $p < 0.05$ ) of both river flows was observed in 2003, as well as a significant increasing shift occurred in 2012 ( $4.1 \text{ m}^3 \text{ s}^{-1}$  and  $7.5 \text{ m}^3 \text{ s}^{-1}$  at Foglia and Metauro, respectively,  $p < 0.05$ ). Altogether, the low-flow regime extended from 2003 to 2012 in both rivers.

The river discharges showed a clear seasonal cycle, with a dry season in late spring-summer and a wet season in winter-autumn (Fig. 7a and b). Discharges usually peaked in February and March, with mean values of  $13.5$  and  $28.7 \text{ m}^3 \text{ s}^{-1}$  for the Foglia and the Metauro, respectively. The driest periods were generally July-September and June-August, respectively, with mean values of  $3.1 \text{ m}^3 \text{ s}^{-1}$  for the Foglia and  $5.9 \text{ m}^3 \text{ s}^{-1}$  for the Metauro.

According to the aggregated data, the precipitation regime in 1997-2019 showed a significant increase only in the Metauro area ( $+0.95\% \text{ year}^{-1}$ ). According to the seasonal data, precipitation increased in winter ( $+4.45\% \text{ year}^{-1}$  and  $+5.14\% \text{ year}^{-1}$ ) and spring ( $+2.44\% \text{ year}^{-1}$  and  $+2.41\% \text{ year}^{-1}$ ) in the Foglia and the Metauro areas, respectively, and decreased significantly in summer and autumn in both areas by about  $2.0\% \text{ year}^{-1}$  in summer and by  $-4.3\% \text{ year}^{-1}$  (Foglia) and  $-1.49\% \text{ year}^{-1}$  (Metauro) in autumn (Table 1).

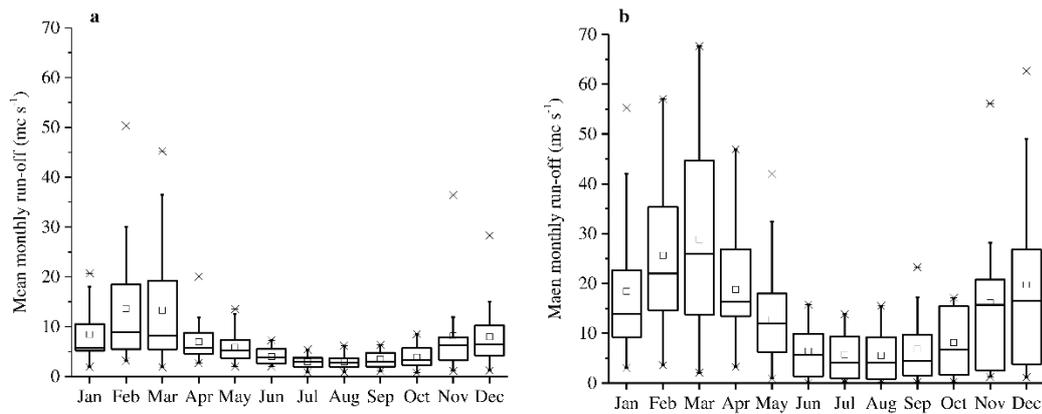


Fig. 7. Seasonal cycle of monthly runoff of the Foglia (a) and the Metauro (b) rivers in 1997-2019. The box plots report the data distribution with mean ( $\square$ ), median (-), interquartile range (box), non-outlier range (vertical bars) and outliers (\*). Data provided by Marche Region and Servizio di Protezione Civile.

#### 3.4. Nutrient loads

Based on the aggregated data, the nitrate and phosphate loads, expressed as  $\text{tons month}^{-1}$ , decreased significantly in both rivers, nitrate by about  $2.61\% \text{ year}^{-1}$  and phosphate by about  $4.65\% \text{ year}^{-1}$  in both rivers, whereas the silicate load showed a significant increase ( $2.18\% \text{ year}^{-1}$ ) in the Foglia (Table 2). The seasonal nitrate and phosphate load generally exhibited decreasing trends, with the exception of the nitrate loads, which increased significantly in winter and spring in both rivers, and the phosphate trend of the Metauro, which was not significant in winter. Based on the seasonal data, the silicate load showed an upward trend in winter-spring and a downward trend in summer-autumn in both rivers. The latter finding is in line with the seasonal runoff and precipitation trends of the two rivers.

**Table 2.** Variation (% year<sup>-1</sup>) of nitrate, phosphate and silicate loads (tons month<sup>-1</sup>) at Foglia and Metauro rivers in 1997-2019. Data were estimated by Generalized Linear Model (GLM) regression. ns: not significant ( $p > 0.05$ ).

Parameter (tons month <sup>-1</sup> )	Variation (% year <sup>-1</sup> )				
	Aggregated data	Winter	Spring	Summer	Autumn
Foglia Transect					
Nitrate	-2.39	+3.99	+3.63	-5.33	-8.25
Phosphate	-4.38	-2.92	-5.38	-7.80	-3.80
Silicate	+2.18	+4.60	+5.47	-3.68	-3.08
Metauro transect					
Nitrate	-2.84	+3.82	+3.46	-5.32	-5.92
Phosphate	-4.92	ns	-6.88	-10.58	-5.31
Silicate	ns	+4.47	+4.58	-4.87	-3.52

## Discussion

We analyzed the physical parameters (temperature and salinity), Chl *a*, and nutrient (nitrate, phosphate, and silicate) data collected at two coastal stations in front of the Foglia and Metauro Rivers (North-western Adriatic Sea) in a 23-year data series (1997-2019). The annual and seasonal trends mostly showed a common pattern at both sites, with exception for discharges and nutrient loadings mainly due to the different hydrographic capacities of the two rivers.

Surface temperature lacked a significant temporal (both annual and seasonal) trend and was highly variable. At the two stations close to the coast, the data reflected the typical characteristics of coastal ecosystems, by low water column depth and consequently with more vertical mixing (Kralj et al., 2019; Raicich and Colucci, 2019; Vilibic et al., 2019). The higher water hydrodynamics in proximity of the coast strongly influences oceanographic properties and can mask seawater warming, which has been documented in the same area (Russo et al., 2002; Brunetti et al., 2006). In particular, temperature showed the typical seasonal cycle of temperate areas, with maximum in summer ( $29 \pm 0.01$  °C in August) and minimum in winter

( $4.8 \pm 0.01$  °C in January) at both sites. As regards salinity, its reduction according to the annual as well as the seasonal data was consistent with the increased discharges of the two minor rivers found in the study area, the Foglia and the Metauro. The reduction was more marked in winter and spring, in relation to the larger plume close to the coast (Marini et al., 2015). In the north-western Adriatic Sea, a similar downward trend has been described by Totti et al. (2019) in a period that was part of the 23-year dataset investigated in this study. In other Adriatic coastal areas, the minor river discharges seem to play a more important role than the plumes of the major river, as in the Gulf of Trieste (Cozzi and Giani, 2011; 2012). In our study area, salinity was affected by the seasonal cycle and showed higher values in summer, lower values in autumn and winter, and a marked variability in spring.

The aggregated and seasonal data both reflected decreasing Chl *a* and nutrient trends at the coastal strip stations throughout 1997-2019, with exception, the increasing Chl *a* trend at the Foglia in spring. The downward trend of Chl *a* may be related to lower nitrate and phosphate loads in the two rivers, as also been reported in other areas of the northern Adriatic after 2000 (Cozzi and Giani, 2011; Giani et al., 2012). The local decline of surface Chl *a*, emerging from our aggregated data, is also partly in line with information recorded in the northern Adriatic Sea, where decreasing Chl *a* concentration seemed to be influenced by reduced Po River discharges and nutrient loads, roughly from 2000 to 2010, due to nutrient-limiting conditions and reduced rivers discharges due to drought (Maric et al., 2012; Totti et al. 2019). The decline was more consistent on the western eutrophic region than on the eastern side of the Adriatic Sea, whose oligotrophic features can also be detected in satellite data at the basin scale (Melin et al., 2011; Colella et al., 2016). Remarkably, the Chl *a* decline was paralleled by reduced phosphate loads (Solidoro et al., 2009; Alvisi and Cozzi, 2016). Indeed, EU sewage treatment legislation, introduced in the mid-1980s to restrain nitrate and phosphate river loads, and dwindling freshwater discharges in the Po basin, due to drought, combined to reduce nutrient

concentrations, hence phytoplankton biomass reproduction, in the northern Adriatic Sea (Mozetic et al., 2010). However, analysis of our dataset did not highlight a consistent relationship between coastal water properties and the magnitude of the Po discharges and nutrient loadings (data not shown), which flow southward with the WAC (Grilli et al., 2005; Campanelli et al., 2011; Lipizer et al., 2014). In fact, our study area, which included the Foglia and Metauro transects, was probably more affected by the local geomorphology, as described for other similar stretches of the Adriatic coast (Alberotanza and Zandonella, 2004; Spagnoli et al., 2010; Appiotti et al., 2014; Spagnoli et al., 2014). Only, at seasonal scale, the upward Chl *a* trend seen in spring was related to the higher biomass abundance measured in the last six years of the series (mean values of 2.7  $\mu\text{g L}^{-1}$  and 2.1  $\mu\text{g L}^{-1}$  at Foglia and Metauro transect, respectively). Overall, Chl *a* followed a seasonal cycle where biomass abundance peaked in winter, rather than in spring, was lowest in summer, and showed a second peak in late autumn. These blooms were characterized by monospecific or mixed diatom assemblages, predominantly *Chaetoceros* spp. and/or *Skeletonema marinoi* as the winter bloom species indicators (unpublished data; Cabrini et al., 2012; Totti et al., 2002); these species can rapidly utilize surface nitrate, as demonstrated by the negative trend of surface nitrate described in this and other studies (Zavatarelli et al., 1998; DeGobbis et al., 2005; Grilli et al., 2020). Analysis of our dataset demonstrated highly abundant and variable phytoplankton biomass blooms in January-February (Duarte et al., 2000; Bernardi-Aubry et al., 2006; Gle et al., 2007; Alvarez et al., 2009; Zingone et al., 2010) and suggested that the winter blooms were triggered and supported by low water column depth (10-12 m), homogeneity of vertical phytoplankton distribution (data not shown), seawater column stability, and resuspended nutrient availability (Townsend et al., 1994; Fischer et al., 2014). However, it is plausible too that some episodic coastal blooms in 1997-2019 were also supported by nutrients from the Po discharges or that they actually originated in the Po basin and were later carried down the western coast by the

WAC (Jeffries et al., 2007). Thus, the algal blooms in this area may be supported either by the discharges and nitrate and phosphate loads of the Po and the minor rivers or by the discharges and nutrient loads of the minor local rivers alone (Penna et al., 2004; Marini et al., 2008; Campanelli et al., 2011).

In 1997-2019, the downward trend of surface nitrate and phosphate was probably affected by lower local nutrient inputs (Foglia and Metauro). This would also agree with the oligotrophication of the northern Adriatic Sea, described mainly in the 1990s and 2000s, as a result of reduced surface nitrogen and phosphorus concentrations and decreased Po River nutrient loadings, which in 2003-2007 fell by 50-70% (Giani et al., 2012). Clearly, the areas farther from the Po delta are more likely than those closer to it to become oligotrophic due to reduced nutrient transport and/or greater nutrient deficiency (Volf et al., 2013). Our data suggests that the nutrient loading of the two minor rivers influenced the biogeochemical properties, including chlorophyll *a*, of the local coastal area (Suppl. Tables 3 and 4). According to the aggregated data, local nitrogen and phosphate loads decreased. The improved water plant treatment of urban and domestic wastewater introduced by the EU (e.g., the Urban Wastewater Treatment Directive, 91/71/EEC), considerably reduced phosphate loads and concentrations in coastal waters (Viaroli et al., 2018; Volf et al., 2018). It now appears that the detergent legislation of the 1980s and the limitations imposed on phosphate-based fertilizers effectively reduced the phosphate inputs in the northern Adriatic Sea. In addition, the Nitrates Directive (91/676/EEC) reduced nitrate use in agriculture to reduce eutrophication. Nitrate reduction is also an integral part of the Water Framework Directive (2000/60/EC), which set up hydrographic districts and whose aim is to achieve a good status for all European water bodies. Finally, the reconversion of livestock and industries also aims at reducing the impacts of nutrient loads on river basins (Garrido-Lestache et al., 2005). Notably, in 1993-2015, the Po River nitrate and phosphate loads showed significant decreasing trends (Grilli et al., 2020). As

regards the nutrient loads, their downward trend in the northern Adriatic is the result of several factors, including river discharge variability due to alternating long periods of drought and high flows and to water withdrawal for use in human activities. In fact, also in our study area, the seasonal trends indicated that precipitation and nutrient loads seemed to be influenced by climate, since winter and spring were characterized by high rainfall and increased nutrient (nitrate and silicate) loads. By contrast, strong drought in the summer and autumn of 1997-2019 strongly reduced nutrient loads to the sea, resulting in lower annual nutrient values. The hypothesis that climate change favors extreme seasonal events, i.e., high rainfall in winter-spring and drought in summer-autumn (Brunetti et al., 2001; Caporali et al., 2021), is clearly confirmed by our seasonal data.

According to the aggregate and the seasonal data, the trends of surface and river silicate loads were not significant. They showed a high variability in 1997-2019, with a steep reduction in 2003 and 2007, when extreme drought conditions reduced the silicate loading and water discharges of the Foglia and Metauro (data not shown). It is likely that silicate release in river drainage basins and eventually in coastal waters is largely a natural process caused by weathering rocks and sediments rather than by precipitation and sewage discharge (Malej et al., 1997).

An irregular distribution of precipitation through the year is typical of the Mediterranean climate. Prolonged drought in summer is followed by intense precipitation that is more frequent in autumn and winter. In addition to snow melt in the Alps and Apennines in spring, winter and autumn rainfall is a major forcing factor in river regimes and affects oceanographic properties (Cozzi et al., 2012). Therefore, in the Adriatic Sea freshwater discharges significantly depend on precipitation, which may be affected by climate change (Soto-Navarro et al., 2020). The Foglia and Metauro discharges increased significantly in 1997-2019 according to the aggregated data, reflecting the seasonal cycle characterized by higher flows in

winter and spring and lower discharges in summer and autumn. Thus, the increasing annual winter and spring trends accounted for the rising discharges of both rivers. This river flow variability was also reflected in the mean annual freshwater discharges of the Foglia and Metauro, which showed alternating higher (1997-2002 and 2013-2019) and lower (2003-2012) flow regimes. The low-regime flow culminated with a significant shift in 2003, and the lowest freshwater discharge in 2007. Low-water periods, documented in the same years also in the Po and in some minor northern Adriatic rivers, were attributable to severe prolonged droughts which substantially reduced their flow rate in 2003-2012 (Lloyds-Hughes and Saunders, 2002; Giani et al., 2012; Lipizer et al., 2012). It has been noted that marked climate variability can induce extended low-water phases alternating with high-rainfall periods and a high frequency of floods (Viaroli et al., 2018).

The annual precipitation variations recorded by the Foglia and Metauro pluviometric stations close to the coast showed a pattern similar to the one of the river discharges; in particular, the aggregated data showed a significant annual percent increase in the Metauro area, whereas the seasonal data showed a significant increase in winter-spring and a significant decrease in summer-autumn both in the Foglia and the Metauro areas. The climate variability in the subregional scale may have played a major role in this marked seasonality. Thus, prolonged summer droughts were followed by autumns that no longer provided high flow rates. The clear seasonal cycle of the Foglia and Metauro discharges can be related to the seasonal climate variations, with high runoff fed by snow melt and rainfall in winter until May alternating with low-flow months in summer until October, the early autumn being characterized by scarce runoff, probably due to low rainfall.

Altogether, the freshwater discharges and rainfall data indicate that the precipitation regime is a major forcing factor regulating the biogeochemical dynamics in this coastal ecosystem of the north-western Adriatic Sea (see also Cozzi et al., 2019).

## Conclusions

Analysis of a multi-year environmental and biological data series indicated that the North-western Adriatic coastal areas are affected by strong anthropic pressures and by climate change. According to the seasonal data, high winter-spring rainfall periods alternated with summer droughts that were exacerbated by dry autumns. Climate instability therefore resulted in highly variable local freshwater discharges and nutrient (nitrate and silicate) river loads. River loads were higher in winter-spring and markedly lower in summer - autumn. Seawater temperature did not show an upward trend either in the aggregated or in the seasonal data due to shallow water mixing, which disturbed the coastal water system. The significant downward trend of salinity in the aggregate as well as the seasonal data was probably due to the high river discharges in winter-spring, but also to minor atmospheric events that in summer-autumn hampered water mixing and allowed it to stay longer in the coastal area.

The EU legislation, regulating wastewater treatment and the agricultural use of fertilizers, reduced nitrate and phosphate loadings, with marked effects on coastal ecosystem productivity. A tendency toward oligotrophication may be attributed to the downward interannual surface nitrate and phosphate trends determined by declining nitrate and phosphate loads. Notably, the lower nutrient availability agreed with the downward Chl *a* trend. Although these coastal areas receive direct river outflows, the oligotrophic conditions documented in the North-western Adriatic Sea by other authors were apparent here too.

River discharge dynamics is a major forcing factor affecting the biogeochemical properties of the northern Adriatic coastal ecosystem in the interannual scale. Despite the major influence of the Po waters on coastal and offshore systems, data analysis indicated that minor river discharges have the potential to influence biogeochemical conditions. This aspect agrees with the role played by the other minor rivers in the oceanographic properties and ecosystem

characteristics of the northern Adriatic Sea. The river discharge and nutrient loading trends described herein were consistent with changed climate conditions and the use of continental waters for human activities. The marked decline in phosphate and nitrate transport and their reduced loads in coastal waters are leading to still persisting oligotrophic conditions in this coastal Adriatic ecosystem.

### **Acknowledgements**

This study has received funding from the EU Interreg Italy-Croatia WATERCARE Project 2019 (Water management solutions for reducing microbial environment impact in coastal areas - Grant 10044130); from University of Urbino and Regione Marche Project of coastal monitoring n. 49 of 23/12/2013 (Table C).

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## LEGEND TO THE FIGURES

Figure 1. Sampling stations in the North-western Adriatic Sea. The stations were located along two transects, respectively in front of the Foglia (F) and the Metauro (M) rivers, at 0 m (river mouth), 500 m (F500, M500) and 3000 m (F3000, M3000) from the coast.

Figure 2. Aggregated data trends of surface a) temperature ( $^{\circ}\text{C}$ ), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) and f) silicate ( $\mu\text{M}$ ) at the Foglia and Metauro transects in 1997-2019. Red line: long-term trend with 95% confidence limits that were shown by gray lines. The slope represents the annual increase or decrease percentage per each variable. The long-term regression is not reported when the slope was not significant ( $p > 0.05$ ).

Figure 3. Seasonal trends of surface a) temperature ( $^{\circ}\text{C}$ ), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) and f) silicate ( $\mu\text{M}$ ) at the Foglia transect in 1997-2019. Red line: long-term trend with 95% confidence limits that were shown by gray lines. The slope represents the annual increase or decrease percentage per each variable. The long-term regression is not reported when the slope was not significant ( $p > 0.05$ ).

Figure 4. Seasonal trends of surface a) temperature ( $^{\circ}\text{C}$ ), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) f) silicate ( $\mu\text{M}$ ) at the Metauro transect in 1997-2019. Red line: long-term trend with 95% confidence limits that were shown by gray lines. The slope represents the annual increase or decrease percentage per each variable. The long-term regression is not reported when the slope was not significant ( $p > 0.05$ ).

Figure 5. Mean annual cycle of surface a) temperature ( $^{\circ}\text{C}$ ), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) and f) silicate ( $\mu\text{M}$ ) at the Foglia transect in 1997-2019. The box plots show the data distribution with mean ( $\square$ ), median (-), interquartile range (box), non-outlier range (vertical bars) and outliers (\*).

Figure 6. Mean annual cycle of surface a) temperature ( $^{\circ}\text{C}$ ), b) salinity, c) chlorophyll *a* ( $\mu\text{g L}^{-1}$ ), d) nitrate ( $\mu\text{M}$ ), e) phosphate ( $\mu\text{M}$ ) and f) silicate ( $\mu\text{M}$ ) at the Metauro transect in 1997-2019. The box plots show the data distribution with mean ( $\square$ ), median (-), interquartile range (box), non-outlier range (vertical bars) and outliers (\*).

Fig. 7. Seasonal cycle of monthly runoff of the Foglia (a) and the Metauro (b) rivers in 1997-2019. The box plots show the data distribution with mean ( $\square$ ), median (-), interquartile range (box), non-outlier range (vertical bars) and outliers (\*). Data provided by Marche Region and Servizio di Protezione Civile.