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Analysis of a comprehensive monthly dataset on nitrogen, phosphorus and organic carbon in the Venice lagoon waters (Italy)

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Abstract
Data on dissolved nitrogen, phosphorus and organic carbon concentrations recorded in the waters of the Venice Lagoon, covering a period spanning from 2007 to 2019, has been subjected to statistical analysis meant to evaluate seasonality, spatial variability and trends. The analysis revealed the role of the complex morphology, hydrological features and anthropogenic sources in determining the water quality and the dynamics of the ecosystem.Long-term trends were in line with the picture of the general enhancement of the chemical status of the lagoon observed in the last decades. Further improvements might be achieved dealing with the issues of the untreated effluent discharge in the canals of the urban centre and the agriculture fertilisers coming from the drainage basin and transported by the freshwater tributaries. The collection of such temporal data series has revealed the effectiveness to detect both short and long-term changes in the water quality. The maintenance of such temporal data series will be a useful tool for evaluating future changes arising from the climate change.

Keywords
Nutrients, Organic carbon, Temporal trends, Spatial variability, Venice Lagoon

Introduction

The Venice Lagoon has a long history of extensive human intervention covering about ten centuries and this uninterrupted work has been undergoing until the present days. During the nineteenth century, the industrialisation of the western shore of the lagoon has caused the deterioration of the chemical and ecological status of the lagoon. The big raise of nitrogen and phosphorus loads due to the direct release from chemical plants, linked to the production of ammonium compounds and fertilisers, as well the agricultural development of the drainage basin, combined with the alteration of hydrological features, were at the root of dystrophic crisis that affected the lagoon in the past.

Since the 1970s a legal framework consisting of a number of national laws and ministerial decrees has been established with the aim of protecting Venice and its lagoon from natural and human-induced hazards. In the 1990s new environmental sensibilities and stricter environmental regulation modified the institutional framework establishing very strict limits for industrial effluents to lagoon waters and banning the discharge of several toxic, persistent and bioaccumulative contaminants. In order to implement

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the regulatory framework, census and controls of water discharge have been conducted and systematic monitoring activity has been established. Among the pollutant species monitored were trace elements, persistent organic pollutants and nutrients (Berti et al., 2020; Berti et al., 2021). The collection of data from this constant monitoring activity allows us to have time series to perform test hypotheses regarding environmental changes.

In this study we focused on nitrogen, phosphorus and organic carbon concentrations in the waters, measured in the framework of the monitoring programs. Data records (2007-2019 for N, 2008-2019 for P, 2008-2015 for C) were studied for seasonality, spatial variability and temporal trend.

Long-term changes of nutrients in the Venice Lagoon have already been investigated in limited areas of the lagoon or different timeframes, highlighting the progressive improvement of the chemical and ecological status (Pastres et al., 2004; Zirino et al., 2016; Sfriso et al., 2019; Acri et al., 2020).

Materials and methods

The Venice Lagoon (VL, 500 km2), located in the Northern Adriatic Sea exhibits a complex morphology characterised by the presence of salt marshes, tidal flats, shoals and navigable channels (mean depth 1.5m). The lagoon receives freshwater from twelve small tributaries (30 m3/s) and the exchange of water with the open sea is driven by semidiurnal tidal fluxes through three inlets (mean tidal range 0.84 m). Detailed bathymetric, hydrologic and salinity features can be found in Ghezzo et al. (2011) and Umgeisser et al. (2014).

Table 1. *Geographic coordinates of sampling sites.*

n.	site	N	E	n.	site	N	E
1	Palude Maggiore	45°30’16.8’’	12°29’17.2’’	13	San Pietro	45°19’37.7’’	12°17’01.0’’
2	Palude di Cona	45°30’25.0’’	12°23’53.1’’	14	Pellestrina	45°16’56.0’’	12°18’04.6’’
3	Burano	45°28’58.1’’	12°25’19.2’’	15	Settemorti	45°16’55.2’’	12°15’13.4’’
4	Campalto	45°28’10.6’’	12°20’07.4’’	16	Valle Millecampi	45°17’41.5’’	12°11’17.9’’
5	Murano	45°27’12.9’’	12°21’21.9’’	17	Canale Novissimo	45°13’31.8’’	12°14’11.6’’
6	S. Giuliano	45°27’37.2’’	12°17’37.0’’	18	Laguna di Lusenzo	45°12’44.7’’	12°17’16.2’’
7	Fondamenta Nuove	45°26’30.5’’	12°20’34.8’’	19	Canale Lombardo	45°11’59.5’’	12°15’54.4’’
8	Rialto	45°26’15.2’’	12°20’05.5’’	20	Adriatico	45°25’49.5’’	12°27’25.0’’
9	Lido - San Nicolò	45°25’59.7’’	12°23’34.6’’	21	Fusina	45°25’6.5”	12°15’34.4”
10	Lago dei Teneri	45°24’02.0’’	12°12’33.4’’	22	Canale Ind. Nord	45°27’24.5”	12°15’37.8”
11	Sacca Sessola	45°24’09.6”	12°19’27.4’’	23	Canale Ind. Ovest	45°27’23.6”	12°14’4.8”
12	Canale del Fisolo	45°21’25.0’’	12°18’01.3’’				

Based upon its characteristics the lagoon has been partitioned into multiple water bodies (WB, figure 1) differing for salinity (Euhaline > 30, Polyhaline 18-30) and for hydrologic parameters (Confined, Not Confined): Euhaline Confined (EC), Euhaline Not Confined (ENC), Polyhaline Confined (PC), Polyhaline Not Confined (PNC). Two more WBs (VLN, VLS) are diked to create fish farms with water exchanges limited and regulated artificially.

The monitoring activity is performed monthly by collecting samples at 22 sites covering the entire lagoon (figure 1 and table 1) excluding areas not subject to tidal excursion (VLN, VLCS WBs). It should be specified that sampling site n. 3 was located at the edge of the PNC2 WB and site n. 19 has been considered in the PC3 even if it laid on the border of ENC3 and PC3 WBs. Two sampling sites (n. 22 and 23) were in the canals of the industrial area (CI)

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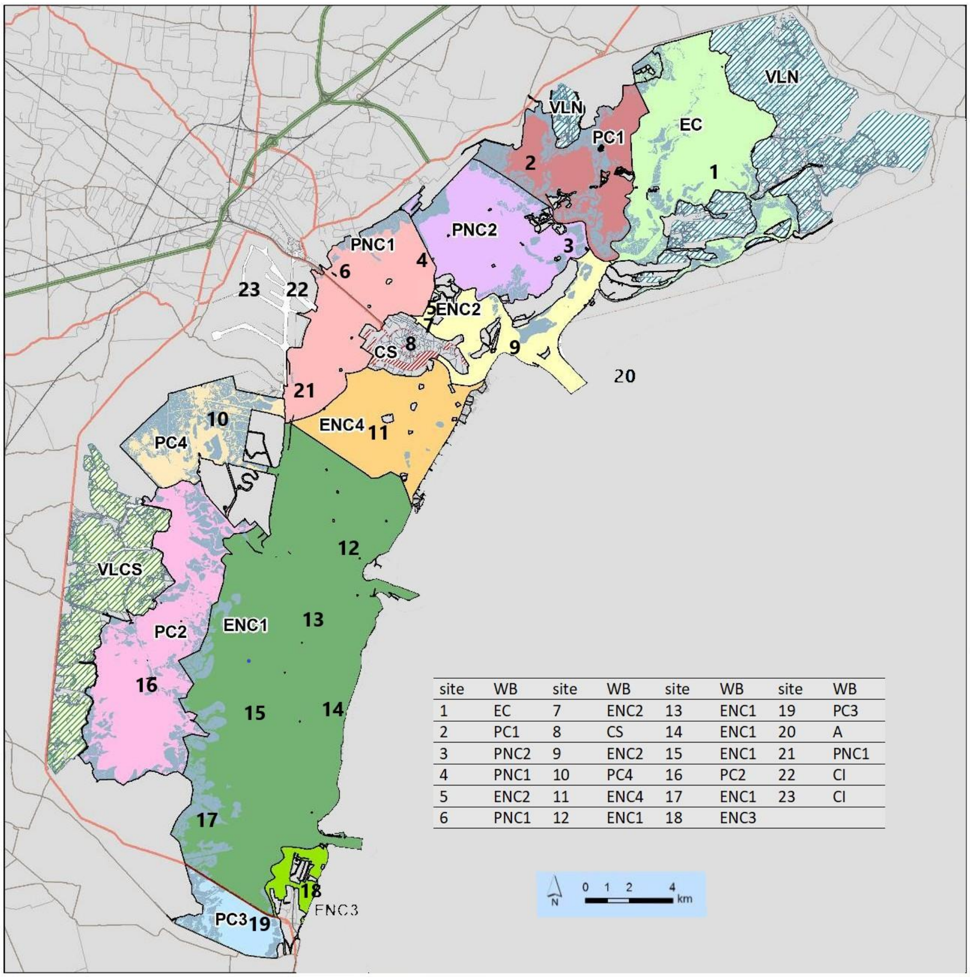
located on the western shore of the lagoon. One sampling site (n. 8) was inside the urban canals of Venice (CS). An additional sampling site (n. 20) was located outside the lagoon in the Adriatic Sea (A). The samples were collected under neap tidal conditions, at 0.5 m depth, during daylight hours.



site	WB	site	WB	site	WB	site	WB
1	EC	7	ENC2	13	ENC1	19	PC3
2	PC1	8	CS	14	ENC1	20	A
3	PNC2	9	ENC2	15	ENC1	21	PNC1
4	PNC1	10	PC4	16	PC2	22	CI
5	ENC2	11	ENC4	17	ENC1	23	CI
6	PNC1	12	ENC1	18	ENC3		

Figure 1. *Study area with the water bodies represented and the position of the sampling sites.*

Analytical determinations were performed in accordance with APHA AWWA WEF Standard Methods.

Total and dissolved organic carbon (TOC, DOC) were measured as carbon dioxide after heated-persulfate oxidation method (APHA AWWA WEF 5310 C), by using a nondispersive infrared (NDIR) analyser (Aurora 1030, OI Analytical). The detection level was 40 μM C. Dissolved carbon was determined after in situ filtration by using 0.45 μm pore size polyethersulfone membranes.

For the determination of nitrogen and phosphorus species the water samples were in situ filtered by using a bottle-top vacuum filter system with cellulose acetate membranes of 0.45 μm pore size (Corning). Samples were kept frozen (-20° C) until they were analysed.

Nitrogen species and orthophosphate were determined spectrophotometrically by using a segmented flow analyser (FLOW IV, OI Analytical) as specified in APHA AWWA WEF 4130.

Total dissolved nitrogen (TDN) was determined as nitrate after heated-oxidation of nitrogenous compounds in an alkaline medium with persulfate sodium hydroxide (APHA AWWA 4500-P-J). Dissolved inorganic nitrogen (DIN) was determined as the sum of ammonia, nitrates and nitrites, while dissolved organic nitrogen (DON) as difference between TDN and DIN.

Total dissolved phosphorus (TDP) was determined

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spectrophotometrically after the heated-persulfate oxidation method of phosphorus compounds under acid conditions (APHA AWWA WEF 4500-P J) by using a discrete analyser (Ganimede P, Hach Lange). In the discrete analyser, an aliquot of the sample is digested and subsequently analysed as P-PO_4^{3-} (APHA AWWA WEF 4500-P F).

The detection levels were 1.4 µM for N-NH4$^+$, 0.2 µM for N-NO_2^-, 3.6 µM for N-NO_3^-, 7.1 µM N for TDN, 0.2 µM P-PO_4^{3-}, 0.3 µM for TDP.

The reported detection levels (DL) shall be understood as minimum reporting levels according to the terminology of APHA AWWA WEF Standard Methods (APHA AWWA WEF 1010 C).

The analytical performances were annually checked through proficiency testing exercises (Quasimeme programmes AQ1).

Records were statistically analysed using non-parametric tests (Helsel and Hirsch, 2002). In order to assess the differences between records Kruskal-Wallis (KW) test was applied. At each sampling site Mann–Kendall trend (MK) test was applied to determine whether a trend has occurred (Hirsch et al. 1991; Yue et al., 2002; Mozejko, 2012). Whenever the seasonal cycle was present in the data, seasonal Kendall test (SK) was applied (Hirsch and Slack, 1984). To determine whether a consistent pattern of trend occurs across the entire lagoon, at multiple locations, the Regional Kendall test for trend (RK) was applied (Helsel and Frans, 2006). Concentrations lower than DL were set at half of the limit. The statistical analyses performed for this study were considered significant at a p-value of less than or equal to 0.05.

Spatial variability has also been investigated performing a cluster analysis (Kaufman and Rousseeuw, 1990) considering each station as an object in order to seek similarities between observations. A matrix consisting of median data of variables for each station, standardised using median and interquartile range, was calculated to input in the algorithm. The cluster analysis has been performed comparing different unsupervised agglomerative hierarchical methods, calculating for each analysis the agglomerative coefficient, which measures the amount of clustering structure found.

Statistical and clustering analysis were performed using R version 3.6.1.

Results and discussion

The main results are summarised in table 2 where quartiles, expressed in µM, are reported. In figure 2 box plots of data grouped by WBs were depicted, representing the median, the 25th and 75th percentiles (lower and upper hinges) and the interval within 1.5-fold the interquartile range (lower and upper whiskers). Values exceeding the whiskers have been hidden.

The median concentration of dissolved organic carbon (DOC) in the VL was 125 µM C. Higher concentrations were measured at the sampling sites located in PC WBs (n. 2, 10 and 16), whose medians were about 200 µM C, with the exception of sampling site n.19 located in PC3, in the southern lagoon, whose DOC level was lower (median of 158 µM C). Lower values of DOC were recorded at the sampling sites located in ENC WBs whose medians ranged between 83 µM C and 117 µM C, with the exception of three sampling sites located in the southern lagoon (n. 15, 17, 18) characterised by medians of 150, 167, 146 µM C respectively. Intermediate concentrations were measured at the sampling sites located in PNC

Table 2. *Quartiles expressed in µM*

Qs	N-NH_{4+}	N-NO_{3-}	N-NO_{3-}	DIN	DON	TDN	P-PO_4^{3-}	TDP	DOC	TOC
0	<1.4	<3.6	<0.2	<5.2	<7.1	<7.1	<0.2	<0.3	<40	42
25	2.1	4.0	0.36	8.6	10	24	<0.2	<0.3	92	117
50	4.7	13	0.71	19	15	35	<0.2	<0.3	125	167
75	9.4	26	1.2	38	22	57	0.52	0.65	175	216
100	193	477	14	511	465	692	7.9	9.2	658	749

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WBs where medians between 133 μM C and 158 μM C were observed (sites n.3, 4, 6), with the exception of sampling site n. 21 in the PNC1 WB, characterised by a lower median (117 μM C). Intermediate concentrations were also observed in the EC WB (site n. 1) located in the northern lagoon (median of 142 μM C). At station n.8 located in the urban canals the DOC median was 117 μM C, while at the two sites located in the industrial canals (n. 22, 23) the DOC medians were 117 μM C and 175 μM C respectively. The dissolved form dominated the organic carbon pool accounting to about 80% of the TOC whose median was 167 μM C.

Organic carbon showed seasonal variability, confirmed by KW test when the data were grouped by months ($p<0.001$). The median concentrations of DOC and TOC reached a peak in spring (180 μM C and 240 μM C respectively) before decreasing during summer and falling down to minimum values in winter (DOC: 100 μM C, TOC: 120 μM C). Variation of the organic carbon concentrations was accompanied by a modification of the dissolved fraction (DOC/TOC ratio) ranging from 86% in winter to 77% in late spring.

The KW test indicated a statistically significant difference in DOC concentrations when the data were grouped by years in 17 out of the 22 sites located in the lagoon. Trend test (MK or SK) applied at each site showed a statistically significant decreasing trend with estimated rate of change ranging between -6.9 μM C per year and -12.6 μM C per year. The analysis extended to a regional scale confirmed a statistically significant difference among years (KW test, $p<0.001$) and significant decreasing trend (RK test, $p<0.001$) with an estimated rate of change of -9.1 μM C per year.

The median concentration of dissolved nitrogen (TDN) in the VL was 35 μM N. About half of this was inorganic nitrogen (DIN), nitrates representing the predominant form. A marked degree of spatial variability of nitrogen species was observed linked to hydrodynamic conditions and local inputs such as sewage discharge or freshwater river. Higher concentrations of dissolved nitrogen were recorded in the industrial canals (site n. 23) and at the sampling site located in the urban canals of Venice (n. 8) where TDN medians were 92 μM N and 73 μM N respectively, 70% of TDN was inorganic forms (DIN). Both sampling sites were affected by anthropogenic sources. At the sampling site located in the urban canals, contribution from inputs carrying inadequately treated sewage effluents led to the disturbance of the nitrogen species ratios with a much higher contribution of ammonium (54% of DIN) whose median was 28 μM N. Higher concentrations of dissolved nitrogen were recorded at the sites located in the polyhaline confined bodies PC1, PC4 as well, where TDN median was 69 and 64 μM N respectively. In these two WBs DIN was 69 and 67% of TDN respectively and ammonium accounted for 20% of DIN. Fairly variable levels of N were observed in the records of the stations located in the PC3, PC2 WBs and those in the PNC WBs with TDN medians ranging between 32 and 44 μM N. Lower concentrations of N were observed at the site records of euhaline water bodies where medians of TDN ranged between 19 μM N and 31 μM N with the exception of sampling site n.7 and n.17 in which were found TDN medians of 38 μM N and 34 μM N respectively. Site n.7 was located close to the city of Venice and was probably affected by urban sewage effluents. At these two sampling sites, ammonium accounted for 36% of DIN.

Dissolved inorganic nitrogen species showed a well-defined seasonal pattern, confirmed by KW test when the data were grouped by months ($p<0.001$). The lowest DIN values were measured during the summer season (median of 6 μM N), while waters with higher DIN values were observed in winter (median of 40 μM N). Variation of the DIN concentration was accompanied by the modification of the ratios of the different nitrogen forms. In winter the contribution of nitrates to the inorganic nitrogen pool was 80% and ammonium was 20%, meanwhile in summer these contributions were 50% and 46% respectively. Nitrites ratio didn't vary significantly, never exceeding 5% of DIN. Dissolved organic nitrogen (DON) showed an opposite seasonal trend with a peak in summer (median of 20 μM N) and levels reduced by half in winter. As a consequence, TDN levels dropped in early spring (from about 50 to 30 μM N) and remained steady throughout the summer until late autumn. It is noteworthy to point out the irregular pattern of ammonia at site n.8 which differed from seasonality possibly due to the disturbance of the sewage effluents.

MK test has been applied for trend. A significant decreasing trend has been found at only 4 sites (1, 11, 14, 21) for ammonium and at 5 sites (5, 9, 21, 22, 23) for nitrates. Nitrites showed a significant difference among years (KW test) at 10 sites but a significant

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decreasing trend could be detected at just 4 sites of them (1, 21, 22, 23), while at two sites the rates of change were positive (n.5 +0.012 μM N per year, n.8 +0.027 μM N per year). As regards the sum of the inorganic species (DIN) a significant difference in concentrations when the data were grouped by years were detected at 8 out 22 sites located in the lagoon (KW test, $p<0.05$), showing a statistically significant decreasing trend when trend test was applied (SK test, $p<0.01$) with estimated rates of change ranging between -0.46 μM N per year at site n.11 and -2.7 μM N per year at site n. 23. The KW test indicated a statistically significant difference in DON concentrations when the data were grouped by years at just 3 out of 22 sites (12, 21, 23), and only one of these (n. 21) showed a statistically significant decreasing trend (MK test, $p<0.05$). The analysis extended to a regional scale confirmed a statistically significant difference among years (KW test, $p<0.001$) as well as a significant decreasing trend (RK test, $p<0.001$) for both DIN and TDN with an identical estimated rate of change (-0.46 μM N per year), whereas the hypothesis of no trend could not be rejected for DON.

Fifty percent of phosphates and total dissolved phosphorus (TDP) measurements performed in the VL were lower than the DL (0.2 μM P and 0.3 μM P respectively). At the sampling sites located in the EC and ENC WBs the median of P measurements was lower than the DL as the percentages of values lower than the DL reached eighty percent, with the exception of the sampling sites n. 7 and 18. At the site n. 7 the median of P-PO_4^{3-} was 0.47 μM (13% of measurements < DL) while TDP was 0.55 μM P (14% < DL). At site n.18 the observed medians were 0.23 μM for P-PO_4^{3-} and 0.36 μM P for TDP (32% P-PO_4^{3-} < DL, 41% TDP < DL). Both of which were probably affected by urban sewage effluents. As already observed for nitrogen, the highest concentrations of P were detected at the sampling site located in the urban canals of Venice (n.8), where the median of P-PO_4^{3-} and TDP were 2.1 μM and 2.3 μM P respectively, as well as at the site n. 23 located in the industrial canal (1.5 μM for P-PO_4^{3-} and 1.6 μM P for TDP). Moreover, WBs with higher levels of P were PC1, where median of 0.58 μM and 0.65 μM P were observed for P-PO_4^{3-} and TDP respectively, and PC4 where the medians were 0.65 μM (P-PO_4^{3-}) and 0.81 μM P (TDP). In the other two PC WBs (PC2, PC3) P medians were lower than the DL. Fairly variable levels of P were observed in the records of the stations located in the PNC WBs. At the station n.3 (PNC2) median of both P-PO_4^{3-} and TDP were lower than DL, at the station n.4 (PNC1) median of P-PO_4^{3-} was lower of DL and median of TDP was 0.36 μM P; levels of P recorded at the stations n.6 and n.21 of the PNC1 WB were higher: 0.61 μM for P-PO_4^{3-} and 0.74 μM P for TDP at site n. 6, 0.52 μM for P-PO_4^{3-} and 0.61 μM P for TDP at site n. 21.

When the data were grouped by months the differences between groups were statistically significant (KW test, $p<0.05$) at 14 out of 22 sampling sites for P-PO_4^{3-} and at 9 sites for TDP ($p<0.05$). At the sampling sites located in the ENC WBs the monthly changes were not clearly identifiable due to the high number of measurements lower than DL. Narrowing down the examination on records characterised by higher levels of P, well above the DL, such as those regarding sites n.2 (PC1), n.10 (PC4) and n.6 (PNC1), the temporal evolution of P over the months could be seen more clearly, characterised by increasing levels over spring, reaching the peak in May (0.92 μM for P-$PO_4^{3-}$and 1.02 μM P for TDP at site n. 2), followed by a drop off in summer with minimum values in July and August (0.26 μM for P-PO_4^{3-} and 0.42 μM P for TDP at site n. 2) and intermediate concentrations during autumn and winter.

KW test indicated a statistically significant difference in both P-PO_4^{3-} and TDP concentrations among years. Trend tests (MK or SK) applied at each site showed a statistically significant decreasing trend for P-PO_4^{3-} at 8 records. At three of those the estimated slope was equal to zero as a consequence of ties in the record due to the presence of a high number of values lower than the DL. At the other five sites (n.2, 10, 18, 21, 22) the estimated rate of change varied between -0.018 μM and -0.057 μM per year. For TDP decreasing trends were detected at 9 sites, three of which with slope equal to zero. At the sites n. 2, 10, 18, 21, 22, 23 the rates of change were between -0.024 μM P and -0.065 μM P per year.

The N/P ratio is commonly used to describe the relative importance of N and P as factors limiting primary production. N/P ratio is usually calculated from DIN and P-PO_4^{3-}, but some authors argued that TDN and TDP provide better estimates of bioavailable N and P (Zirino et al., 2016). Taking into account only records characterised by measurable P levels (n. 2, 6, 7, 8, 19, 18, 21, 22, 23) and excluding those most affected by anthropic effluents (n. 8 and

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23), the median relationship between N and P in the Venice Lagoon was 64 to 1 by atoms in the first case (DIN/P-PO_4^{3-}). Considering TDN and TDP the median ratio was 86, ranging from 66 at site n.6 and 120 at site n.2, and following a seasonal pattern (KW test, $p<0.001$) with lower values in summer (TDN/TDP = 49) and higher values in winter (TDN/TDP = 113). The hypothesis of no trend cannot be rejected at any site with the exception of site n. 18 and 21 where significant positive trends were detected (SK test, $p<0.001$) with an identical estimated rate of change (+4 per year).

In view of the previous results the VL can be considered a P-limited system, in accordance with Zirino et al. (2016).

The output of the cluster analyses provided indications for the identification of spatial patterns among the sampling stations. In figure 3 is depicted the dendrogram using Euclidean distances as metric for distance calculation and Ward as linkage rule which gave the best agglomerative coefficient (0.91) among those considered (values closer to 1 suggest strong clustering structure).

Observing the dendrogram, two couples of stations associated in the same cluster were clearly separated from the others. The first couple consisted of the sites located in urban and industrial canals (n. 8, 23) both of them affected by effluent discharges and characterised by limited hydrodynamics of the canal network that increase the retention of substances.

The second couple consisted of sites n. 2 and 10 located in PC1 and PC4 WBs respectively. Both are located close to the mainland and confined by a belt of saltmarshes from the central lagoon, PC1 bearing also the input of a tributary river.

From the remaining stations a cluster consisting of stations most influenced by the water exchange with the Adriatic Sea and characterised by lower water renewal time (Umgeisser et al., 2014) could be identified (n. 11, 12, 13, 14) strictly associated with the site n.9 located at the northern inlet and the sampling station located outside the lagoon (n.20). Another cluster consisting of stations located on the landward side of the lagoon emerged from the clustering (n. 1, 3, 4, 5, 15, 16, 17, 18, 19). These sites, characterised by higher water renewal time, were affected by tributaries discharge, outfalls from fish farms and runoff from the mainland. A group of stations located in the central lagoon (n. 21, 22, 6, 7) matched to each other. Site n. 6 was located close to the mouth of a river running through the large urban settlement which extends inland. Site n. 7 was affected by domestic waste water, being located close to the city of Venice. Sites n. 21 was located on the western shore of the lagoon facing the industrial zone while site n.22 was located in the industrial canals.

The result of the cluster analysis appeared to be in good accordance with the classification proposed by Solidoro et al. (2004) based on data acquired between 2000 and 2003.

Comparison with other lagoons is questionable due to the wide variability of the hydrodynamical features of each lagoon such as the water renewal time, water flushing time and mixing efficiency (Umgeisser et al., 2014), let alone the different human drivers affecting them. However, some general features regarding seasonal variability and spatial gradients are common characteristics in Mediterranean lagoons (Roselli et al., 2009; Specchiulli et al., 2008; Specchiulli et al., 2018).

Barrón C and Duarte C. M (2015) compiled an inventory of DOC concentrations in coastal locations. DOC levels found in this survey in PC WBs were comparable to the median value reported for vegetated coastal waters (180 μM C) that included coastal lagoons (Barron and Duarte, 2015), meanwhile levels found in ENC WBs appeared to be more similar to the median reported for open coastal zone (111.3 μM C), confirming the high variability of chemical parameters arising from the presence of heterogeneous environments in the Venice Lagoon.

The Marano-Grado Lagoon (MGL, 160 km^2) is part of the extended transitional system network of the northern Adriatic Sea basin, which includes the VL as well. The two lagoons have a similar tidal range (0.90 vs 0.85 m) but MGL has a lower water renewal time (3.0 vs 10.4 days) coupled with a higher mixing efficiency (Umgeisser et al., 2014). The MGL is also less affected by anthropic activities. Nevertheless, it is characterised by a much higher amount of freshwater discharge (70 vs 30 m^3/s). In the MGL the median concentrations for ammonia and nitrite (3.16 μM N, 0.70 μM N respectively), found in a monitoring campaign performed between 2013 and 2014 (Acquavita et al., 2015), were similar to those found in VL. Nitrates varied following the common seasonal pattern observed elsewhere (higher in winter, lower in summer) with a median of 31.4 μM N (Acquavita et al., 2015), higher than the medians observed in the same years in the VL (18 μM N and

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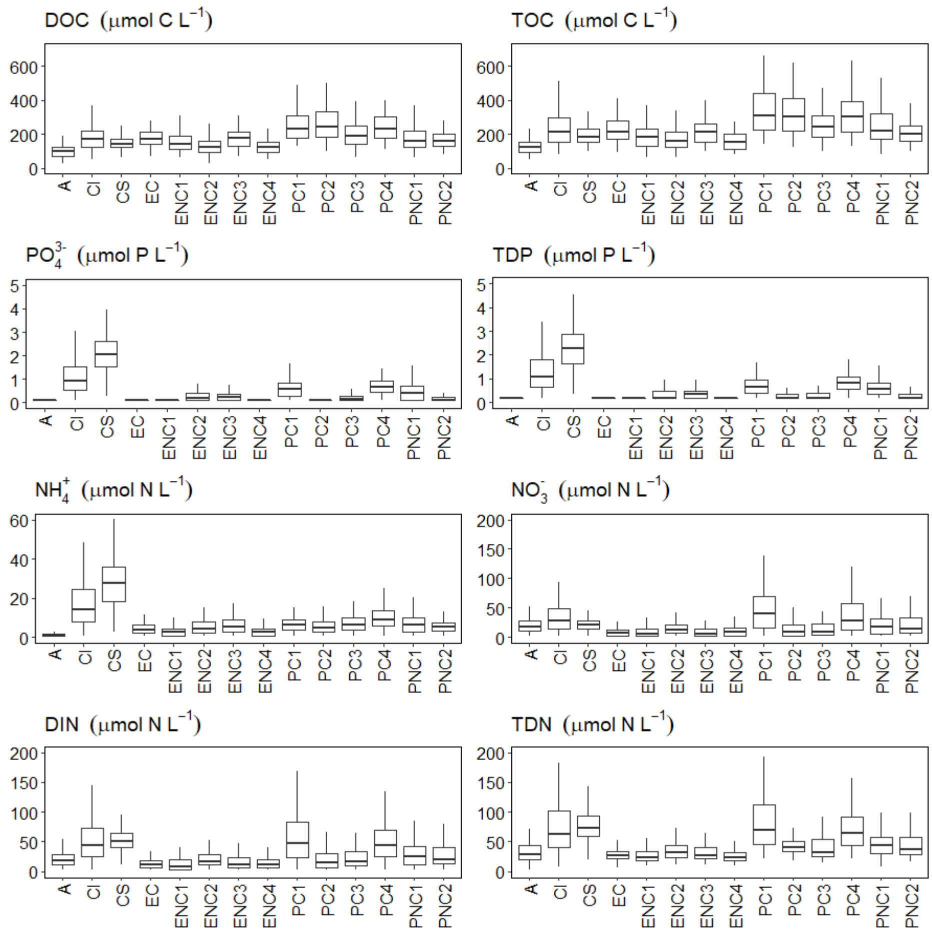

Figure 2. *Box plots of data grouped by water bodies*

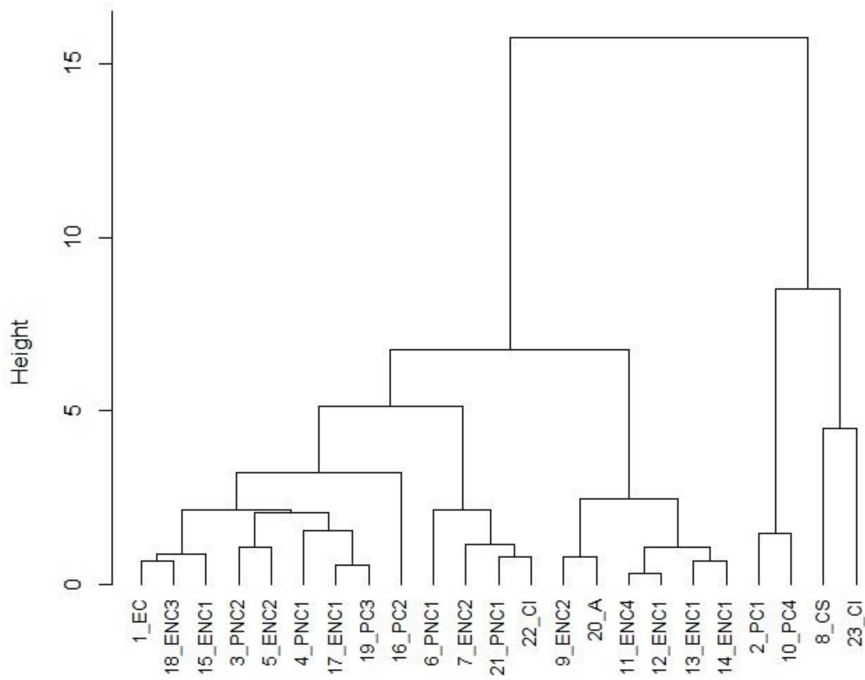

Figure 3. *Dendrogram of the Cluster Analysis obtained by using Ward as linkage rule and Euclidean distances as metric for distance calculation between sampling sites*

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17 μM N for 2013 and 2014 respectively). For soluble reactive phosphorus a median of 0.08 μM P has been reported. Based upon the N/P ratio both lagoons are P-limited.

In the past, the VL was affected by massive macroalgal blooms, occurring mainly in the eighties, as a consequence of elevated levels of nutrients coming from direct industrial emissions as well as drainage basin loads. These blooms were frequently followed by anoxia in large areas of the lagoon triggering huge fish die-off and sulphide emissions. In the last decades the VL has undergone improvement of the water quality by making such phenomena less frequent. Nevertheless, episodes of algal bloom are still possible, such as that which occurred in the central lagoon in 2013. This event has been linked by some authors to the large amounts of nutrients rich freshwater coming from over-snowed mountains (Bastianini et al., 2013). That year the DIN median was 62 μM N in January, 68 μM N in February and 32 μM N in March. But rather than follow the typical descendant seasonal gradient, because of the thaw DIN level peaked again up to 68 μM N in April. By comparison the median DIN in April of the considered temporal frame was 18 μM N. The high level of nitrogen (Fig. 4) brought the algal species to flourish during the early summer leading to the development of an extensive hypoxic area. The event reached the final stage on 19th and 20th July, during the Redentore celebration, with a huge fish die-off accompanied by the release of sulphide which, with a terrible stench, poisoned the air in the Venice town and surroundings.

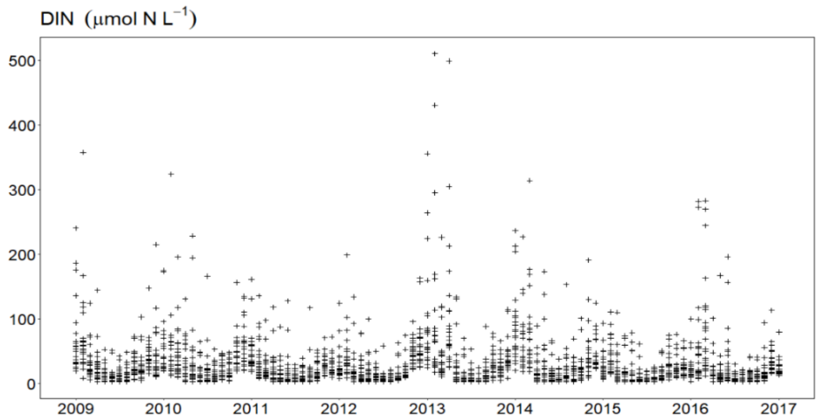

Figure 4. *Scatterplot of dissolved inorganic nitrogen mesaurements*

Conclusions

The analysis of a comprehensive data set on nitrogen, phosphorus and organic carbon in the waters of the Venice Lagoon, collected during monitoring campaigns from 2007 to 2019, has revealed the effectiveness of such monitoring programmes to detect rapid change in water quality, like that occurred in 2013, when higher levels than normal of nitrogen during winter and early spring were recorded, triggering anoxia crisis in the summer, as well as long term trends in line with the general improvement of the lagoon observed since the 1990s upon the implementation of stricter environmental regulation. Further accomplishment concerning the ecological status of the lagoon might be earned by taking on the issue of the urban discharge coming from the sewers flowing directly into the urban canals, considering that the historical centre is almost completely lacking a sewerage system (Libralato et al., 2012). Moreover promising outcomes might arise from projects aimed at restoring the typical ecotonal environment of the lagoon (Sfriso et al., 2021, Feola et al., 2022).

The collection of long-term monitoring records of water quality parameters is essential to notice significant changes that are taking place in coastal waters, even more so for an ecosystem like the Venice Lagoon that has a long history of human intervention that is still undergoing nowadays. At the seaward inlets, an impressive engineering work consisting of a complex system of gates (MOSE), designed to prevent the city of Venice from surging due to exceptional tides, first came into operation in October 2021.

The maintenance of this temporal data series is also a certainly valuable tool for researchers to shed light on the effects driven by climate change. There is evidence that warming episodes might have a direct influence

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on the primary productivity of the lagoon (Bertolini et al., 2021). The modification of the precipitation regime might significantly affect the fraction of nutrients transported from the drainage basin to the lagoon leading to the alteration of the seasonal nutrient pattern and variation in the phytoplankton community (Pesce et al., 2018). Furthermore, the sea-level rise combined with the necessary increase of closures of the seaward inlets (Lionello et al., 2021) are expected to limit the sea-lagoon water exchange, mostly in the autumn-winter months, increase the water renewal time and decrease the flushing capacity of the lagoon, especially in its central part (Ferrarin et al., 2013). The water chemistry of the lagoon is closely tied to the hydrological conditions given that the output of toxic substances and degradation products of the organic matter is driven by the exchange with the sea.

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