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# Nitrogen to phosphorus ratio in the Venice (Italy) Lagoon (2001–2010) and its relation to macroalgae



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#### ABSTRACT

Analysis of the annually-averaged 2001-2010 monthly nutrient data from 13 stations in the Venice Lagoon (Italy) shows that the concentrations of dissolved nitrogen (N) species, measured as total dissolved N (TDN), have increased over time while that of phosphorus (P) species, measured as total dissolved P (TDP) have decreased. During the study period, the TDN/TDP ratio in the lagoon rose from about 46:1 to 100:1 (by atoms), a level at which the growth of benthic macroalgae is favored over that of sea grasses. The increase of the TDN/TDP ratio appears to be caused by two factors: (1) a small, but increasing amount of N in river water entering the lagoon, and (2) low P input combined with adsorption and entrapment of orthophosphate on colloidal iron oxides and carbonates at the water-sediment interface. This second mechanism would explain the increase in the TDN/TDP ratio, principally in zones of low salinity, where hydrodynamic residence times are long enough to permit N enrichment and result in macroalgal growth preferentially in the central, landward, side of the lagoon. However, an examination of the algal coverage of the lagoon floor from 2002 to 2010, indicates that while macroalgal abundance may be influenced by the N/P ratio, the spatial and temporal distribution during this period cannot be explained solely by this one feature. Nonetheless, this work points to the importance of considering the contributions that sediments in shallow lagoons make to the over-all system productivity and ecology and may be applicable to other shallow environments.

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#### 1. Introduction

During the last 60 years, the concentrations of nitrogen (N) and phosphorus (P) present in the Venice (Italy) lagoon have been the object of many studies (Marcomini et al., 1995; Pastres et al., 2004; Cossarini et al., 2008; Solidoro et al., 2010; Facca et al., 2011). More recently, large quantities of these nutrients have led to a proliferation of benthic macroalgae that peaked in the mid to late 1980s and decreased markedly with the banning of P discharges in the lagoon, in 1989. The principal sources of N and P into the lagoon were, and still are, river inflows, direct urban and industrial discharges, submarine groundwater discharges (SGD) and (less quantified) from atmospheric aerosols and gases. Rough estimates of total N and P input into the lagoon are  $6.4 \times 10^3$  metric tons/year of N and  $4.5 \times 10^2$  metric tons of P. These load estimates have been independently confirmed by

multiple studies (Zirino, 2005; Sfriso et al., 2005; Facca et al., 2011) and suggest that N and P inputs and over-all primary production have been approximately constant over the 2001–2010 period.

From the late eighties to about 2006, the lagoon experienced declining macroalgal growth and coverage, as evidenced from surveys (Sfriso and Marcomini, 1996; Sfriso et al., 2003; Curiel et al., 2004). This reduction was principally caused by 1) the banning of phosphatebased laundry detergents and 2) reduced light penetration caused by the suspension and re-suspension of sediments in the central lagoon by fishermen using illegal clam-harvesting practices. However, from late 2006 to 2010 there occurred a renaissance of Ulva sp. concentrated in the central lagoon in 2007 (Magistrato alle Acque, Venezia. (MAV) – MAV-Corila-CNR ISMAR (2009)); and in the southern lagoon in 2009-2010 (MAV-SELC (2010)). In The year 2009 resulted in an overall increase of both angiosperms and macroalgae in the lagoon over the previous 4-5 years (MAV - Corila-CNR ISMAR (2009); MAV-SELC (2010)). Nevertheless, while the sea grass coverage of the lagoon has been relatively constant from 2004 to 2008, registering only a small increase in 2009, macroalgal coverage increased and shifted from the central lagoon, between the historical city of Venice and the mainland, to that portion of the lagoon that lies between the Malamocco



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and Chioggia entrances. Although the increase in macroalgae was never close to 1980s levels, it is still worrisome because in summer blooms of *Ulva* sp. and *Vaucheria* may decompose overnight, resulting in a local loss of oxygen and release of toxic hydrogen sulfide into the water column (Solidoro et al., 2010). Especially concerning is the formation of large patches of *Ulva* just southwest of the historical city of Venice, an area that was not heavily populated by *Ulva* between 2002 and 2005, but known to become anoxic in the past (Fig. 1).

The 2000 to 2010 period has also been a period of regular lagoon monitoring, primarily through the Monitoraggio dell'Ecosistema Lagunare (MELa) programs carried out by the MAV via its principal contractor, the Consorzio Venezia Nuova (CVN). Because an abundance of N over P in shallow estuaries is well known to foster macroalgal growth (Harlin, 1995; Valiela et al., 1997; Bricker et al., 2008), the purpose of this work was to examine the 2000–2010 data on the N and P concentrations in the Venice Lagoon in an effort to determine the causes that led to the recent proliferation of macroalgae. Our principal hypothesis is that the abundance of macroalgal coverage of the lagoon floor is related to the dissolved N/P ratio of the water, and that this ratio is being increased by the selective retention of P over N in the sediments. In this work, we have taken total dissolved nitrogen (TDN) as a measure of available N and total dissolved P (TDP) as the measure of available P (*vide infra*).

#### 2. Methods

#### 2.1. Study site

The Venice Lagoon is very wide but shallow; its area to depth ratio is approximately  $550 \times 10^6$  m<sup>2</sup> to 1.5 m, and points out the importance of sediments and (potentially) atmospheric sources in regulating the "chemistry" of the water (Markaki et al., 2010). The lagoon is separated from the Gulf of Venice and Adriatic Sea by reinforced longshore sand bars. There are three openings: the Lido entrance to the north, which is about 1.6 km wide, the narrower Malamocco entrance at the center (<1 km), and the Chioggia entrance to the south, also <1 km. Normally, the lagoon is well flushed by the tides and well mixed vertically by both bottom friction and wind action, and therefore, mostly well oxygenated (Solidoro et al., 2010). Hydrodynamic residence times vary from 1 to 3 days near the entrances to 20-30 days in the least flushed sectors adjoining the mainland (Guerzoni and Tagliapietra, 2006). The lagoon floor is etched with many narrow channels, but the main ones, leading from each of the entrances to the mainland, are of significant depth (ca. 20 m) and wide enough to accommodate supertankers and the largest ocean liners. It is estimated that approximately 50% of the water flow in and out of the lagoon travels via the channels. Throughout, there are extensive mud flats that become exposed at low tide.



Fig. 1. Location of stations and river/channel dischargesdiscussed in this work. MELa stations sampled monthly and/or bimonthly are shown only by number or name. The historical city of Venice is found at Station Ve-4 (FN). "Ve" stations that adjoin MELa stations, but collect data *in situ* every 30 min are not discussed in this work. Channels are named and connected to their discharge points by straight lines. Areas that were predominantly occupied by macroalgae in May–June 2007 (but not before 2005) are shown in green. The red star shows the approximate location of the ARPAV (Gulf of Venice) samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Average tidal range is approximately  $\pm$  35 cm, with large excursions occurring under seasonal Bora (NE) or Scirocco (S–SW) wind conditions. The lagoon receives freshwater discharges principally from 12 sources comprised of major tributaries plus several minor rivers and a number of managed channels (Collavini et al., 2005). Freshwater discharge is regulated and is relatively consistent year round (Zuliani et al., 2005). Due to the historical diversion of much of the river inflow around the lagoon, the average freshwater input rate is believed to be only a few percent of the input rate of Gulf of Venice water (200 m<sup>3</sup>/s. vs. 10,000 m<sup>3</sup>/s) (Gacic et al., 2002; Gacic and Solidoro, 2004). However, the accuracy of this estimate is undermined by the presence of largely unquantified volumes of submarine groundwater discharges (SGD's) (Rapaglia, 2005; Ferrarin et al., 2008; Garcia-Solsona et al., 2008; Rapaglia et al., 2010).

Salinity data from 2000 to 2009 indicate that the lagoon encompasses distinct zones of differing salinities, consistent in both space, season, year (Solidoro et al., 2004; Zirino et al., 2014), and residence times (Ghezzo et al., 2011). Infaunal data indicate that the lagoon can be divided into (at least) three discrete ecosystems, labeled as (freshwater) Source, Intermediate, and Marine (Tagliapietra and Sigovini, 2009). This classification essentially divides the lagoon into three parallel zones along its major axis. Because of the negative correlation between salinity and hydrodynamic residence times (Zirino et al., 2013) this partitioning is more robust than the historical division of the lagoon into three zones perpendicular to the major axis. The Venice Lagoon with its inlets of rivers and canals, and outlets to the Gulf of Venice and Adriatic Sea, is shown in Fig. 1.

#### 2.2. Monitoring program

Data for this study were obtained from the MELa (1-5) programs (MAV-CVN, 2002-2010). With the exception of 2006, when economic restrictions prevented the collection of water quality data, the individual MELa programs spanned from September 2000 to December 2010, and initially aimed for maximum spatial coverage of the lagoon with the MELa 1 sampling program being the most complete. MELa 1 consisted of 31 stations distributed across the lagoon, plus two "baseline" stations located just outside of the Lido and Malamocco entrances. The measurements performed included 19 water quality variables related to eutrophication (temperature, salinity, dissolved oxygen, pH, redox potential, turbidity, chlorophyll-a and phaeopigments, total suspended solids, nitrogen as NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>,  $NO_2^-$ ,  $NO_3^-$ , total inorganic nitrogen (TIN), total dissolved nitrogen (TDN), phosphorus (as  $PO_4^{3-}$ ), total dissolved phosphate (TDP), carbon as total organic carbon (TOC), particulate organic carbon (POC), dissolved organic carbon (DOC)), and seven heavy metals: Cu, Hg, Pb, Zn, Cd, Cr, and Ni plus As. Over nine years, the program was gradually reduced to 24 stations, only 13 of which were part of the original 31 (Zirino et al., 2014). Most of the remaining stations were located in the central lagoon; the others were chosen to give a reasonable areal coverage of the remaining space (Lovato et al., 2013). A second monitoring network called SAMANET (for Sezione Antiinquinmento Magistrato alle Acque – NET) was established by the MAV in 2003 and at present consists of ten automatic monitoring stations located at or near the sites of most of the 13 remaining MELa stations (Ferrari et al., 2008). Additional salinity data (via CTD) are available through the SAMANET monitoring program and correspond well to the MELa data. Because SAMANET data does not include nutrients, it was not used in this study. Nevertheless, the close correspondence between salinities as measured by each program extends the importance of mixing processes to all chemical variables (Zirino et al., 2014). While the MELa data set includes many of them, this study deals only with the concentrations of TDN and TDP made at the 13 "permanent" stations over the 2000-2010 period. Fig. 1 shows their location.

#### 2.3. Procedures

#### 2.3.1. Chemical analysis

Samples were collected from a small vessel using the best oceanographic "clean" techniques (Bruland et al., 1979; Cutter and Bruland, 2012), filtered through a 0.45 µm filter and quick frozen until analysis could be performed in the laboratory. Total dissolved nitrogen (TDN) and total dissolved phosphate (TDP) were analyzed as TIN (NO $_2^-$  + NO $_3^-$  + NH $_4^+)$  and PO $_4^{3-}$ after oxidation with potassium persulfate (CNR-IRSA, 2003). Classical methods, slightly modified by Italian agencies were used. TIN was measured spectrophotometrically after Cd-column reduction and complexation of the resulting (total) NO<sub>2</sub><sup>-</sup> with sulfanilamide/ $\alpha$ naphtyethylenediamine (CNR-IRSA, 2003). Reactive P, or orthophosphate was also measured spectrophotometrically after forming the blue phosphomolybdenum complex (ICRAM, 2001). Analyses were performed during different periods by two laboratories that claimed widely different limits of detection (LoD). For this work we have chosen to use the higher limits for all of the data: TDN = 10  $\mu$ g/L or 0.7  $\mu$ M/L; PO<sub>4</sub><sup>3-</sup> = TDP = 5  $\mu$ g/L or 0.2  $\mu$ M/L. When measured values were below the LoD, the LoD value was assigned. We define the pertinent variables as follows:

 $TIN = NO_2^{-} + NO_3^{-} + NH_4^{+}$ 

TDN = TIN + DON(dissolved organic nitrogen)

 $TDP = PO_4^{3^-} + DOP(dissolved organic phosphorus).$ 

We calculated the N/P ratio from TDN and TDP because 1) they provide analytically robust estimates of bioavailable N and P; 2) in a shallow lagoon,  $NH_4^+$  is a significant source of nitrogen; 3) DON in the main, is available to planktonic microbiota (Berman and Bronk, 2003); 4) we expect the DON/DOP ratio to be similarly distributed as TDN/TDP and 5) TDP is the analog to TDN (Lomas et al., 2009) and its use, in place of  $PO_4^{3-}$  limits scatter and ensures that the TDN/TDP ratio is not overestimated.

#### 2.3.2. Data analyses

The dataset consists of measurements made at the 13 stations once a month (twice a month during some spring months). When two surveys were made within a month the average of the two values was assigned to that month. Measurements were initiated in September 2000 (MELa 1) and ended in December 2010 (MELa 5). The dataset consisted of approximately 1350 measurements distributed over 10 years and four seasons. We defined the samples collected from December 1st to February 28 or 29 as "winter" data, samples collected from March 1st to May 31st as "spring" data, samples collected between June 1st and August 31st were classified as "summer" samples and "autumn" samples were those collected between September 1st and November 30th. Occasionally, due to inclement weather during winter months, not all stations could be sampled. Omissions were few, however, and when they occurred, the calculated seasonal averages included only two months. Sampling at station FN started in January 2004. Station 20B was not sampled in 2009 and 2010. Ten-year averages and standard deviations of TDN and TDP at each station are plotted in Fig. 2. To test for differences between seasons, the quotient TDN/TDP was computed for the entire data set and transformed logarithmically. The transform was found to be approximately normal, with 70% of all points residing between  $\pm$  one standard deviation of the mean (Fowler et al., 1998). Differences among seasons were tested via one-way ANOVA. Salinity and temporal trends were tested via regression analyses. Statistical relationships (means, standard deviations, and statistical significance) were calculated using GraphPad Prism 6® and Microsoft Excel®.



Fig. 2. Seasonal 2000–2010 station averages of TDN (Blue–left axis) and TDP (Purple–right axis). Average 2000–2009 salinities are shown below station names. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### 3. Results and discussion

#### 3.1. Spatial and temporal variability of TDN and TDP

The 2000–2010 seasonal averages of TDN and TDP measured at the 13 MELa stations in order of their 2000–2009 average salinities, are shown in Fig. 2 (no discrete salinities were measured in 2010). Standard deviations are large, approximately 50% of the means, probably due to the combination of variations in climate, analytical error, and by failing

#### Table 1

Seasonal  $r^2$  values for TDN and TDP vs. salinity, averaged across all stations, from 2000 to 2010 (Station 20B omitted).

	TDN	TDP
Spring	0.831	0.389
Summer	0.439	0.195
Autumn	0.338	0.257
Winter	0.473	0.737



Fig. 3. Annually averaged TDN (diamonds, scale on left) and TDP (squares, scale on right) in the lagoon plotted against the 2001 to 2009 average salinity.

Table 2

"p" values of 2000-2010 seasonal averages.

TDP					
Season	Spring	Summer	Autumn	Winter	Ave. conc. (µM)
Spring	1	0.021	0.066	0.671	0.67
Autumn		1	1	0.08	0.65
Winter				1	0.65
TDN					
Season	Spring	Summer	Autumn	Winter	Ave. conc. (µM)
Spring	1	≪0.02	0.844	≪0.02	38
Summer		1	≪0.02	≪0.02	27
Autumn			1	≪0.02	38
Winter				1	51
TDN/TDP					
Season	Spring	Summer	Autumn	Winter	Atomic ratio
Spring	1	≪0.02	0.461	≪0.02	57
Summer		1	≪0.02	≪0.02	44
Autumn			1	≪0.02	58
Winter				1	78

to correct for tidally-caused shifts (Zirino et al., 2014). Despite this, three features are apparent from a visual inspection of Fig. 2: 1) An inverse seasonal and annual correlation of TDN and TDP with salinity (Table 1 and Fig. 3), 2) There are seasonal differences in TDN but not TDP (Table 2), 3) at no station, nor during any season, do TDN and TDP appear to be at the LOD. As inflow into the lagoon is managed, and a two year (1998–2000) record of tributary discharges into the lagoon shows little seasonal variation (Zuliani et al., 2005), we conclude that the seasonal pattern is caused by light-driven nutrient uptake rather than a difference in freshwater flow.

The annually averaged TDN and TDP station values from 2001 to 2010 averaged across all stations<sup>1</sup> are shown in Fig. 4. TDP was significantly negatively correlated to increasing time ( $r^2 = 0.526$ , p = 0.027), while TDN shows no significant trend with time ( $r^2 = 0.033$ , p = 0.638).

#### 3.2. The TDN/TDP ratio

The annually averaged TDN/TDP ratio from 2001 to 2010 is shown in Fig. 5. At all stations, the ratio has increased from about 46:1 to 100:1 by atoms ( $r^2 = 0.5627$ ; p = 0.02). Similarly, 11 stations out of 13, when examined individually, show a positive, significant (p < 0.02) correlation of annually-averaged TDN/TDP ratios with increasing time (data not shown). The outliers are stations 20B and FN, both of which show anomalous amounts of TDN in winter and were sampled fewer years, namely, eight years for 20B and six years for FN. TDP is relatively constant and independent of season; therefore seasonality depends on TDN. Approximate values of the TDN/TDP ratio, by atoms, are: spring, 57; summer, 44; autumn, 58; and winter, 78 (Table 2). The large difference between summer and winter ratios, points to a significant drawdown of N over P, presumably in support of macroalgal growth.

Because primary productivity in winter is low, winter data tends to be most representative of nutrient input and availability and thus was analyzed in more detail. Log normalized winter data was divided into three groups: freshwater impacted, low salinity, high nitrogen, "Source" stations (1B, 10B, 16B and 7B), "Marine" stations, principally Gulf of Venice-impacted, high salinity, low nitrogen, stations, (3B, 11B, 1 M, 4C, and 14B), and in-between "Intermediate" stations,



Fig. 4. Yearly average TDN (diamonds, scale on left) and TDP (squares, scale on right) concentrations in the Venice lagoon from 2001 to 2010.

with intermediate levels of nitrogen and salinity (6B, 20B, 9B, and FN). The Source stations were selected for analysis because they best reflected the introduction of nutrients, from rivers, canals, and ground water into the lagoon. The Log<sub>10</sub> (TDN/TDP) plot for this subset of data shows a significant positive correlation with time ( $r^2 = 0.514$ , p < 0001; Fig. 6).

#### 3.3. Absolute value of the N/P ratio

The well-known N/P ratio of the elemental composition of marine (oceanic) plankton, known as the Redfield ratio (Redfield et al., 1963), is a statistically proven value of 16 to 1 by atoms (about 7 to 1 by weight). This value, as  $NO_3^-/PO_4^{3-}$ , is also commonly assigned to deep ocean water (Anderson and Sarmiento, 1994). However, the median relationship between N and P in macroalgal coastal environments is closer to 30 to 1 by atoms (Atkinson and Smith, 1983) and is variable in estuarine waters (Lane et al., 2004). Primary production in a body of water with an N/P value under 29 could be nitrogen limited, while a value over 29 would be phosphorus limited (Carstensen et al., 2011). Accordingly, TDN/TDP ratios (Fig. 5) indicate that, on an annual basis, the Venice Lagoon is P-limited, e.g., total primary production is controlled by the availability of P.

#### 3.4. Trends in the TDN/TDP ratio

It is widely recognized that the physico-chemical variables in the Venice Lagoon show a high degree of spatial variability (Solidoro et al., 2004; Ghezzo et al., 2011). It has also been reported recently that the salinity pattern was maintained during the last decade with little alteration (Zirino et al., 2014). For these reasons, any judgment that is made for the entire lagoon must also be based on concentrations of constituents measured at stations that, in total, provide a reasonable areal coverage of this water body. The 13 stations that have been sampled continuously from September 2000 to December 2005, and



Fig. 5. Yearly average TDN/TDP ratio in the Venice Lagoon from 2001 to 2010.

<sup>&</sup>lt;sup>1</sup> Because individual station values do not necessarily represent equal volumes of water, "average" concentrations calculated herein are best taken to be indicators of relative differences in concentration.



Fig. 6. Winter  $Log_{10}$  (TDN/TDP) of low salinity stations (1B, 10B, 16B, 7B) from 2001 to 2010.

from January 2006 to December 2010, make up the longest continuous data base that covers the entire lagoon. Eleven of these stations provide independent confirmatory evidence that the N to P ratio in the waters of the lagoon, as calculated from the TDN to TDP ratio, increased from about 40 to 100 (by atoms) between fall 2000 and winter 2010 (p < 0.02).

The increase in the TDN/TDP ratio inside the lagoon suggests that the freshwater entering the lagoon has also increased its ratio. A recent report by the agency charged with monitoring TDN and TDP (ARPAV, 2011) indicates that from 2001 to 2010, the TDN/TDP ratio of the inflowing water oscillated about a mean value of  $34 \pm 4$  (by atoms) and increased only slightly, at a rate of ~0.79 units/year, to a maximum value of about 42 (Fig. 7). When the TDN and TDP in the freshwater are normalized for the difference in yearly flow and plotted as  $g/m^3/y$ , it is apparent that the increase in the ratio is caused by a rather steady increase in TDN concentration (Fig. 8). Nevertheless the contribution of freshwater to the ratio is small when compared to the average yearly increase inside the lagoon of about 6 units/yr. (Fig. 5). Also, the 11 individual stations show yearly increases that vary from ~3.4 units/yr. (Sta. 1 B) to ~11 units/yr. (Sta. 16B). In summary, the temporal increase in the TDN/TDP ratio inside the lagoon is much greater than the parallel increase in the freshwater input ratio. This suggests that a mechanism exists inside the lagoon that causes the N/P ratio to increase.

Input of Gulf of Venice seawater cannot account for the N/P ratio increase within the lagoon because the TDN/TDP ratio is negatively correlated to salinity. Nevertheless, for comparison with the lagoon, we chose a sampling station in the Gulf of Venice, 500 m from the coast, between the Lido and Malamocco entrances as representative of the entering saltwater (Fig. 1). At this site from 2001 to 2009, the TDN/TDP ratio has remained stable at about 55  $\pm$  11 by atoms (ARPAV, 2002-2011) thereby supporting the hypothesis that a process inside the lagoon is increasing the ratio. When the 2000–2009 TDN and TDP data set is grouped by stations (viz., salinity) and Stations



Fig. 7. TDN/TDP of freshwater entering the Venice Lagoon 2001–2010.



Fig. 8. TDN (diamonds, scale on left)) and TDP (squares, scale on right) in freshwater entering the lagoon (2001–2010); normalized by volume.

20B and FN are not included, a significant negative relationship between TDN/TDP and salinity is obtained (Fig. 9). The ratio decreases approximately linearly from about 75 at low salinities to 45 at the higher salinities. The latter value is similar to that of the ratio in the Gulf of Venice, as it should be, since the high salinity stations are largely composed of water from the Gulf of Venice. Thus, at any one time, the TDN/TDP ratio is a function of local N enrichment, and the degree that inshore water is diluted with offshore water. While the negative gradient with salinity indicates that the principal source of N enrichment lies at the northern end of the lagoon, it does not preclude other, decreasing, sediment sources along the gradient.

# 3.5. Hypotheses regarding the cause of the increased TDN/TDP ratio inside the lagoon

The cause of the TDN/TDP ratio increase in waters of low salinity is not completely evident. Nevertheless, one possible mechanism is that the "pumping" of N-rich ground water, along the shore and into the lagoon would favor a high TDN/TDP ratio (Nowicki and Nixon, 1985; Valiela et al., 1999). However, our results indicate that it is a reduction of TDP, more than an increase in TDN, that accounts for the increase in the TDN/TDP ratio that has occurred since 2001 (Figs. 4, 5).

#### 3.5.1. The removal of phosphate

Di Toro (2001) and Joye et al. (2009) suggest a mechanism whereby the N/P ratio can increase during the remineralization process that occurs at the lagoon floor: primary production in the water column results in organic particles (that contain N, P, and Fe as well as the other elements necessary for life), most of which settle to the seafloor where they are quickly buried and covered by more production. In the



Fig. 9. Average 2001–2009 TDN/TDP in the Venice Lagoon as a function of 2001–2009 average salinity.

sediments, oxygen is consumed via bacterial remineralization which results in anoxic conditions that reduce highly insoluble colloidal and particulate Fe(OH)<sub>3</sub> to much more soluble FeS. As a consequence of remineralization, N, P and Fe diffuse across the sea sediment interface into the water where they are re-oxidized:  $NH_4$  to  $NO_3^-$ , P to  $PO_4^{3-}$ , and Fe<sup>II</sup> to Fe<sup>III</sup>(OH)<sub>3</sub>. Hydrated iron oxide then adsorbs a portion of  $PO_4^{3-}$  and returns it to the sediments.  $NO_3^{-}$  is not adsorbed and is returned to the water column, thereby increasing the N to P ratio in the overlying water. Other mechanisms for the sequestration of P over N are possible (Valiela, 1995; Bergamasco et al., 2003), including preferential adsorption on carbonates (Zhang and Huang, 2007) but the key point is that N is enriched over P. This occurs most effectively in zones that have long(er) hydrodynamic residence times and O<sub>2</sub> concentrations above 1 mg/L (Slomp and Cappellen, 2004). In the Venice Lagoon, the low salinity stations have much longer hydrodynamic residence times than the high salinity stations (approximately 3 days vs. 20-30 days) and their shallowness promotes the vertical mixing of O<sub>2</sub> thereby increasing the rate of formation of Fe-hydroxy colloids at the water-sediment interface, which, in turn, contributes to the increase in the N/P ratio. Sediments from low salinity areas are also higher in carbonates (Lucchini et al., 2002).

#### 3.6. The effect of the increasing TDN/TDP ratio on the growth of macrolagae

The MELa programs, (MELa4 (2007-2009) and MELa5 (2009-2011)) that tracked the development of macroalgal mats in the Venice Lagoon from 2002 to 2010, indicate that the spatial distribution of macroalgae inside the lagoon is not particularly related to the higher TDN/TDP ratios (MAV-Corila-CNR-ISMAR, 2009; MAV-SELC, 2010). In 2002 and 2003, macroalgae were clustered in the southern lagoon, south of the Malamocco entrance and Sta. 3B, a high salinity, low nutrient, and low ratio area, dominated by inflow from the Gulf of Venice. In 2004 and 2005, Ulva coverage in this zone thinned by over 60% and continued to thin in 2006. By 2007, macroalgae in the southern lagoon have been reduced to small patches and the main coverage had shifted to the central lagoon, to a zone just southwest of the historical city and to the low salinity, high nutrient, and high N/P area between Venice and the mainland (Fig. 1). In 2009 and 2010 principal macroalgal coverage returned to the southern lagoon, and coverage was twice that of 2002 and 2003. Thus, our original hypothesis, namely that macroalgal growth is directly related to the TDN/TDP ratio in the water, was not confirmed. Spatial coverage does not necessarily indicate total abundance, however, and it is evident that total macroalgal biomass in the lagoon relates closely to the available nitrogen in the water (Sfriso and Facca, 2007; Sfriso et al., 2003). Nevertheless, the interactions that determine both abundance and distribution of, within, and between macroalgal groups, seagrasses, and their physico-chemical environment are complex (Havens et al., 2001; Curiel et al., 2012) and depend on sediment composition, climate, the pattern of gamete dispersion, tidal currents, and predation, among other factors (Geertz-Hansen et al., 1993; Harlin, 1995; Sfriso et al., 2003; Bergamasco et al., 2003).

In the Venice Lagoon the issue is even more complex because of fishing of the Manila clam (*Tapes philippinarum*) in the central lagoon, defined as the area between the Lido and Malamocco entrances (Pellizzato et al., 2011). Clam production reached maximum levels between 1993 and 2001. The dislodging of the top 20 cm of sediment by mechanical means cleared the central area of macroalgae and increased water turbidity, as noted earlier by Sfriso et al. (2005). Also, the return of macroalgae in 2009 and 2010 to the area between the Malamocco and Chioggia entrances could have been expected, as very high densities of juvenile clams were reported south of Sta. 20B, an area of relatively low salinity, and higher N/P ratios (Pellizzato et al., 2011). This would suggest that local freshwater discharges could also determine macroalgal distributions. A recent report by Bastianini et al. (2013), indicates that a major algal bloom, followed by anoxia and mass fish mortalities, occurred in the central lagoon north of

Venice and even in the canals of the historical city. This bloom was linked to "large amounts of nutrient rich freshwaters coming from over-snowed (sic) mountains". Thus, we can conclude that while the N to P ratio may be an important factor in explaining the proliferation and distribution of macroalgae, it is only one of many "drivers" to be considered.

A recent paper (Facca et al., 2014) that discusses the recovery of the Venice Lagoon between 1987 and 2003 shows that the concentrations of benthic macroalgae, total nitrogen, organic phosphorus, and organic carbon associated with the upper 5 cm of sediments of the central lagoon decline with time. However, the total phosphorus, inorganic phosphorus, and inorganic carbon remain relatively constant over the same time period. The relationship TN vs. TP from Facca et al., (2014) is shown in Fig. 10. Although the time periods between our two data sets overlap only slightly and we are comparing TN to TDN and TP to TDP, nevertheless, when we extrapolate the 1987-2003 data to 2010, the difference between water and sediments is striking (Fig. 10 vs. Fig. 4). This strongly suggests preferential retention of phosphorus over nitrogen in the sediments. Additionally, the 1987-2003 N to P sediment ratio of approximately 6 (by atoms) supports our hypothesis that remineralized P is being sequestered and preferentially retained at the water-sediment interface, while N is released into the water column and advected out of the lagoon by the tides.

The observations made in this work may be applicable to estuarine environments other than Venice. While the clam-fishing operations in the central lagoon are peculiar to this site, our findings are based on data from the entire Venice Lagoon and support the concept that sediments play a dominant role in controlling the productivity and ecology of shallow lagoons.

#### 4. Conclusions

Analysis of monthly data collected from 2000 to 2009 at 13 stations distributed to give a reasonable spatial coverage of the Venice lagoon shows that the TDN/TDP ratio in the water column increased markedly from about 40:1 in 2000 to about 100:1 by atoms in 2009. This increase appears to be caused by the preferential removal of P and cannot be related to the TDN/TDP ratio in the freshwater entering the lagoon from the drainage basin nor to the TDN/TDP ratio in the adjoining Gulf of Venice waters. Therefore, it must reflect processes taking place within the lagoon. Guided by the literature (Valiela, 1995; Di Toro, 2001; Cloern, 2001), we suggest that, in the Venice lagoon, there exists a process in which  $PO_4^{3-}$  ions, jointly remineralized with  $NO_3^{-}$  ions in surface sediments, are trapped by adsorption on colloidal iron oxide, while  $NO_3^$ is not retained. Consequently, the water becomes enriched in N. Such a mechanism would preferentially take place where sediments are also rich in organic matter, namely along the shallow, low salinity, northern shore of the lagoon. Indeed, in the Venice Lagoon, this is the location



Fig. 10. Average TN (diamonds) and TP (squares) concentration in sediments in the central Venice Lagoon, 1987 to 2003.

where N enrichment of the water is greatest. This argument is supported by 1987–2003 data showing that, in the sediments of the central lagoon, the concentration of total P has remained essentially constant while total N over this time period has decreased markedly, likely from suspension/resuspension of sediment caused by clam-fishing operations. The present work was motivated by a hypothesis relating the proliferation of macroalgae in the Venice Lagoon to an increasing N to P (TDN to TDP) ratio in the waters of the lagoon. While an increase in this ratio may indeed affect macroalgal abundance, we must conclude that the changing spatial distribution of macroalgae that has occurred between 2000 and 2009 cannot be explained solely by this mechanism. Nevertheless, our observations indicate that by accumulating a greater fraction of P than N, the sediments may play a dominant role in the productivity and ecology of the Venice Lagoon and other, similarly shallow, environments.

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