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Trends of Nitrogen and Phosphorus in Surface Sediments of the Lagoons of the Northern Adriatic Sea as a Study Case

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Abstract: The analysis of nutrient concentrations in surface sediments is a reliable tool for assessing the trophic status of a water body. Nitrogen and phosphorus concentrations are strongly related to the sediment characteristics but are mainly driven by anthropogenic impacts. The results of the determination of total nitrogen and total inorganic and organic phosphorus in surface sediments of the lagoons and ponds of the northwestern Adriatic Sea (Marano-Grado, Venice, Po Delta, Comacchio Valleys, Pialassa della Baiona) show the merit of this approach. Indeed, when previous data are available, the ratio between the actual and background values can provide useful information on the trophic changes that have occurred in the most recent times, and the results can also explain the conditions present in less studied environments. In this context, numerous studies performed in the Venice lagoon since the second half of the 20th century during different environmental scenarios provide mean concentration ranges and propose the main causes of changes. The results of single datasets available for the other lagoons fall into scenarios that occurred in the Venice lagoon. At present, the most eutrophic basins are Pialassa della Baiona, the Po Delta lagoons and ponds and the Comacchio valleys due to industrial effluents, fish farming and clam harvesting, respectively, whereas the Venice lagoon is now experiencing environmental recovery.

Keywords: surface sediments; nitrogen concentrations; phosphorus concentrations; anthropogenic impacts; environment resilience; transitional water systems; Venice lagoon

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1. Introduction

In transitional water systems (TWSs; lagoons, ponds, deltas, estuaries, fjords), nutrient concentrations in surface sediments are key parameters strictly related to changes of anthropogenic impacts [1–3], mostly eutrophication [3–8], river inputs [9–11] and clam harvesting [12–16]. Since the Second World War, the rapid increases in industrial activities, agriculture, urban centers and tourism have profoundly altered the trophic conditions of the TWS [4,5], and sediments have proved to be an excellent litmus paper of the changes taking place. Indeed, they accumulate nutrients [17,18] and pollutants [19–21], above all, during the death of primary producers and the settlement of suspended particles [22,23].

The lagoon of Venice is the largest TWS in the Mediterranean Sea (549 km^2) and presents the ecological conditions recorded in most of these coastal environments [24]. Data on the nitrogen and phosphorus concentrations in the surface sediments of the whole lagoon have been available since the second half of the 20th century [25–27] and are strongly correlated with the ecological changes observed over time [2]. Until the 1990s, a progressive increase of nutrients in the superficial sediments was observed, especially with regard to phosphorus, mainly due to (i) the production of nutrients by industrial synthesis (phosphates and ammonia); (ii) the draining waters from an areas of ca. 1800 km^2

extensively cultivated with monocultures fertilized with high amounts of nutrients; (iii) the discharge of urban wastewater not yet fully treated from the historic center of Venice, the islands of the lagoon and the city of Mestre and its hinterland [28–30]. In addition, the nutrient increase in the water column and surface sediments [18,31] favored the massive production of nuisance macroalgae [21], which during their degradation, further increased the load of nutrients in the surface sediments. The same impacts, especially the increase in trophy with abnormal development of macroalgae nuisance, also affected other TWSs both in Italy and in many other countries worldwide [5,6].

Later, more extensive studies carried out in 2003 and 2011 showed a significant decrease of these eutrophic substances due to industrial activity's decline, the implementation of water treatment plants equipped with a third stage for nitrogen and phosphorus abatement, the banning of phosphorus from detergent formulations (4–5% of total weight) in 1989 [1] and sediment remobilization during the intense Manila clam harvesting [15]. In 2014 and 2018, two additional extensive nutrient mapping studies were carried out but the data were again unpublished. Since 1987, for the central basin of the Venice lagoon, the TWS most studied due to its greater number of anthropogenic impacts, a greater number of mapping datasets are available for both phosphorus and nitrogen during different environmental scenarios.

On the other hand, there is little information from other TWSs of the Northern Adriatic Sea, data on which are scarce and fragmentary. Indeed, only a few data are available for the lagoons of Grado-Marano (2007) [32], the Po Delta (2008), Pialassa della Baiona (2009) and the Comacchio Valleys (2009) [33]. However, these data, all collected by our research group, are very useful to understand the correlations of nitrogen and phosphorus with the parameters associated with different ecological conditions.

This paper aimed to integrate the knowledge on the nitrogen and phosphorus concentrations in the TWS of the northern Adriatic Sea with particular reference to the Venice lagoon, of which a high number of data is available. The complete dataset allows us to analyze the interactions of nutrients with other sediment characteristics and the ecological conditions of these TWSs as a function of anthropogenic impacts and climate changes. The results allow to understand the roles of these elements as indicators of ecological changes and for forecasting future trends.

2. Materials and Methods

2.1. Description of Study Areas and Sampling Campaigns

The lagoons and ponds investigated in this paper are reported in Figure 1. From the north to the northwestern Adriatic Sea, they are: Marano-Grado lagoon, Venice lagoon, Po Delta lagoons and ponds, Comacchio valleys and Pialassa della Baiona lagoon. The stations sampled in 2003 in the Venice lagoon were selected to study the biomass distribution of macrophytes [34]. All the stations sampled in the Venice lagoon since 2011 and the stations sampled in the other lagoons were selected by the Italian Regional Agencies for Environmental Prevention and Protection. Sampling was carried out to determine the ecological status of TWSs in the framework of the European Water Framework Directive 2000/60/EC by using the biological element "Macrophytes". On this occasion, our research group also collected surface sediments to study some sediment characteristics and nutrient concentrations.

2.1.1. The Venice Lagoon

The lagoon of Venice (45°11′–45°34′ N, 12°08′–12°38′ E) (Figure 1) is the largest and the most studied TWS of the Mediterranean Sea. It is located in the northwestern Adriatic Sea and extends over an area of ca. 549 km^2 accounting for ca. 39% of the total Italian TWSs [24]. The waters have a mean depth of ca. 1.2 m, ranging from a few centimeters in the shallower areas to 15–20 m in the main channels. The water exchange with the sea is mainly driven by tidal action [35]—through the three wide (600–900 m) and deep (12–15 m) inlets of Lido, Malamocco and Chioggia—and accounts for ca. 60% of the total reservoir every 12 h [36], whereas the freshwater inputs (ca. 34.5 $m^3 s^{-1}$) are negligible [37]. This allows a high grain-size difference between the sandy areas close to the inlets where water exchange (ca 19,000 $m^3 s{-}^1$) occurs in a few hours, and the clay chocked areas where water renewal may take 40 days [38]. The lagoon is morphologically separated in three main basins—from the salt marshes of Burano and Torcello in the north and the Malamocco-Marghera canal in the south—showing very different morpho-ecological conditions, the central basin being the most polluted and most affected by anthropogenic impacts.

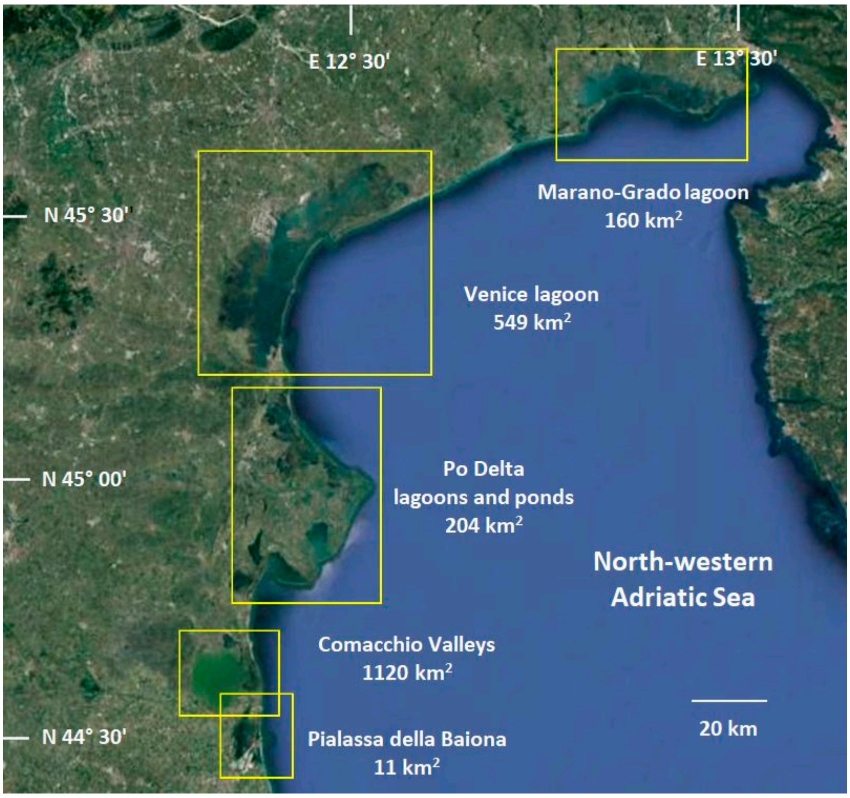

Figure 1. Main transitional water systems (TWSs) of the northwestern Adriatic Sea.

Since 2003, the research team at the Marine Ecology Lab, Ca' Foscari University of Venice (Italy) has collected data on the nitrogen and phosphorus concentrations in the superficial sediments of the entire lagoon. Sampling campaigns were carried out in 2003 (165 stations), 2011 (118 stations), 2014 and 2018 (88 stations), in the late spring to early summer period. In this paper, the concentrations recorded at 85 common stations sampled in all the four surveys are analyzed and compared.

In addition, the concentrations of phosphorus compounds (P_{tot} = total phosphorus, P_{inorg} = inorganic phosphorus, P_{org} = organic phosphorus) were recorded at 34 stations of the central lagoon (132 km^2) in 1987, 1993, 1998, 2003, 2011, 2014 and 2018, during different ecological scenarios that characterized the lagoon since the late 1980s: the dominance of nuisance macroalgae (1987) [18,34]; the decline of nuisance macroalgae (1993) [39]; the intense Manila clam (*Ruditapes philippinarum*) harvesting activities (1998–2003) [15]; the collapse of clam stocks (2011) [2]; the decrease of anthropogenic impacts and the beginning of the lagoon's environmental recovery (2014–2018) [2].

2.1.2. The Lagoon of Marano-Grado

The Marano-Grado lagoon (45°41′–45°46′ N, 13°04′–12°27′ E) (Figure 1) has morphological features similar to those of the Venice lagoon with a surface of ca. 160 km^2 and a tidal difference of 65 cm [36]. It is subdivided in two main basins: The Marano basin, a wide shallow water body characterized by a few islands and tidal-marshes, and the Grado basin, which is rich in morphological reliefs and is shallower than the Marano basin [40]. The average freshwater inflow is ca. 98.5 $m^3 s^{-1}$ [41], whereas water exchange with the sea occurs through three main inlets (Lignano, Porto Buso, Grado) and other smaller mouths. Fine sediments are on average greater at Grado than at Marano and are prevalently calcareous. Information on the nutrient content is scarce. Falace et al. [42] report data for the total nitrogen (N_{tot}) only, with the concentration ranging from 0.5 mg g^{-1} at the sea-inlets, to 1.5 mg g^{-1} at the internal edges. Samples of surface sediments for the analysis of N_{tot}, P_{tot}, P_{inorg} and P_{org} were collected at 20 stations evenly distributed throughout the lagoon in summer 2007.

2.1.3. Po Delta Lagoons and Ponds

The Po Delta (44°09′–45°47′ N, 12°16′–12°32′ E) (Figure 1) has a water surface of ca. 204 km^2 and is sorted into many lagoons and ponds with depths ranging from 0.5 to 2.5 m, according to the water body. Salinity is the most variable parameter due to the many branches of the Po River. Hard substrata are rare and mainly represented by some stone embankments along the edges of the various basins and oyster beds scattered on their bottoms. Clam-farming and clam-fishing activities are very intense and cause high sediment resuspension with severe environmental consequences. The main primary producers of the Po Delta basins are phytoplankton in the areas affected by clam harvesting or free-floating nuisance macroalgae, especially Ulvaceae, Gracilariaceae and Solieriaceae, in the other areas with lower anthropogenic impact. Populations of the aquatic angiosperm *Ruppia cirrhosa* (Petagna) Grande that before the 1990s colonized some basins have now completely disappeared [43]. Samples of surface sediments were collected in 2008 at 20 stations (three at Caleri, two at Marinetta, two at Vallona, three at Barbamarco, three at Canarin, four at Scardovari and three at Goro) during late spring-early summer period.

2.1.4. Comacchio Valleys

The Comacchio valleys (44°55′–44°65′ N, 12°10′–12°25′ E) (Figure 1) are a complex of choked shallow ponds with a surface of ca. 110 km^2, connected with the sea by two small channels that do not allow for sufficient water renewal. They are affected by anthropogenic impacts like fish farming, especially eel farming, and receive freshwater from the Reno River that has shifted the ecological conditions from a good ecological status dominated by aquatic angiosperms and macroalgae of high ecological value, to a degraded and homogeneous basin dominated by phytoplankton and picocyanobacterial blooms of poor-to-bad status [44–46]. Samples for nutrient analyses of surface sediments were collected at two stations, Donna Bona and Dosso Pugnalino, in the main basin during late spring or early summer 2009.

2.1.5. Pialassa Della Baiona

The Pialassa della Baiona lagoon (44°28′–44°31′ N, 12°14′–12°16′ E) (Figure 1) is a shallow basin of ca. 11 km^2 characterized by a mean depth of 60 cm. It is furrowed by a network of herringbone canals, 1–4 m deep, which converge towards the Ravenna harbor connected with the Adriatic Sea. The freshwater inputs, coming from a network of small canals draining an intensively cultivated area, are negligible. The basin is colonized by rich populations of macroalgae, especially the non-indigenous species *Agarophyton vermiculophyllum* [43,47] (Ohmi) Gurgel, J.N. Norris *et* Fredericq. This species covers mostly the southern part of the lagoon with a biomass of 5–10 kg m^{-2} on a fresh weight (fwt) basis. It is a little studied basin characterized by poor ecological conditions [48]. Surface sediments were sampled at three stations—Chiaro Magni, Chiaro Risega and Vena del Largo—in 2009 in late spring to early summer. For this basin, no other samples are available.

2.2. Sediment Sampling

At each station, three subsamples of surface sediments (5 cm top layer) were sampled by a Plexiglas corer (i.d. 10 cm) and mixed together. One subsample (ca. 100 mL) was retained for nutrient (total nitrogen, total phosphorus, inorganic phosphorus, organic phosphorus) analyses and another (ca. 50 mL) for the determination of the sediment density and grain size. Both subsamples were stored at −20 °C until the laboratory analyses.

2.3. Nutrient Determination in Surface Sediments

Information on the concentrations of P_{tot} and N_{tot} in the sediments of the whole lagoon date back to the mid-20th century. The analyses were carried out in the first 30 cm in 1948–49 and 1968–73 and in the first 20 cm in 1983 and 1987–88. In those periods, sediments were collected with a bucket to study the benthic communities [49,50]. During the following years, sediments were collected with a plexiglass corer (i.d. 10 cm) retaining the first 20 cm [27] or 5 cm top layer (this paper). This latter thickness is the sediment most affected by the growth and degradation cycles of macrophytes.

In the laboratory, sediments were freeze-dried and pulverized using a sediment mill (Fritsch Pulverisette, Germany). The concentration of total nitrogen (N_{tot}) was measured in duplicate by a CHNS Analyzer (Vario-MICRO, Elementar CHNS by Elementar Italia S.r.l.) after an accurate sample powdering of ca. 0.3 g of sample. The standard used was "low level N- and S-contents" with N = 0.74%, art. no. 05 000 959.

Total phosphorus (P_{tot}) was determined after sample combustion in the muffle at 550 °C for at least 2 h of 0.3–0.4 g of sample. Subsequently, the residue thus obtained was suspended in 50 mL of 1 N HCl and sonicated for ca. 30 min. After allowing the sample to settle for at least 1 h, 0.5 mL of the supernatant were taken with a graduated gas-chromatographic syringe and brought to exactly 10 mL using volumetric flasks for a final dilution of 1 L, with the result expressed directly in µM. At this point, the phosphorus concentration was determined by spectrophotometry by adding the mixed reagent and reading the absorbance at 885 nm after ca. 10–15 min [51]. Inorganic phosphorus was obtained with the same procedure used for P_{tot} but without combustion at 550 °C. Organic phosphorus (P_{org}) was determined by difference. All samples were analyzed in duplicate and the analyses were replicated on two different days to obtain an accuracy > 95. Otherwise, the analyses were repeated until the coefficient of variation (standard deviation/mean) between two replicates was < 5%.

2.4. Map Preparation

Maps of nutrient distribution were prepared in six concentration ranges by using data collected in the surveys carried out in 2003, 2011, 2014 and 2018. Maps were obtained by Kriging methods using the software R, version 4.0.3, and SAGA, version 2.3.2. Models for each analysis were selected to minimize the prediction errors, and model performances were estimated using cross-validation procedures. Maps were then produced using the software QGIS, version 3.6.0 and integrated into one image using Corel Paintshop Pro X5, version 15.0.0.183 (Corel Corporation, 2012).

2.5. Sediment Characteristic Determination

Dry sediment density (g DWT cm^{-3}) was determined in the laboratory by sediment desiccation at 110 °C in tared crucibles of 20–30 mL. The percentage of Fines (fraction < 63 µm) was obtained by wet sieving ca. 50 g of dried sediment throughout Endecotts sieves (ENCO Scientific Equipment, Spinea, Italy). All analyses were performed in duplicate.

2.6. Statistical Analyses

The analysis of variance (one-way ANOVA) allowed us to test differences of the sediment parameters in different monitoring periods. The differences were considered significant when $p < 0.05$. Prior to the analyses, the distribution of each variable was checked for normality and homogeneity of variance by the Kolmogorov-Smirnov test ($p < 0.05$).

Pearson coefficients ($p < 0.05$, $p < 0.001$) highlighted the correlations among environmental parameters and variables using STATISTICA software, version 10 (StatSoft Inc., Tulsa, OH, USA).

Principal component analysis (PCA), determined using the same software, showed the multivariate patterns of the matrix of 162 cases (stations) and five variables (sediment density, fines, inorganic and organic phosphorus, total nitrogen). The significant loading was considered to be at $p > 0.7$. Moreover, the PCA analysis of the transposed matrix showed the affinity between stations and lagoons.

3. Results

3.1. Nutrient Concentrations and Sediment Characteristics

The mean values of the dry density, the percentages of the fine fraction and the concentrations of nutrients in the surface sediments of the single and total TWSs are reported in Figure 2 and Table S1 (Supplementary Material).

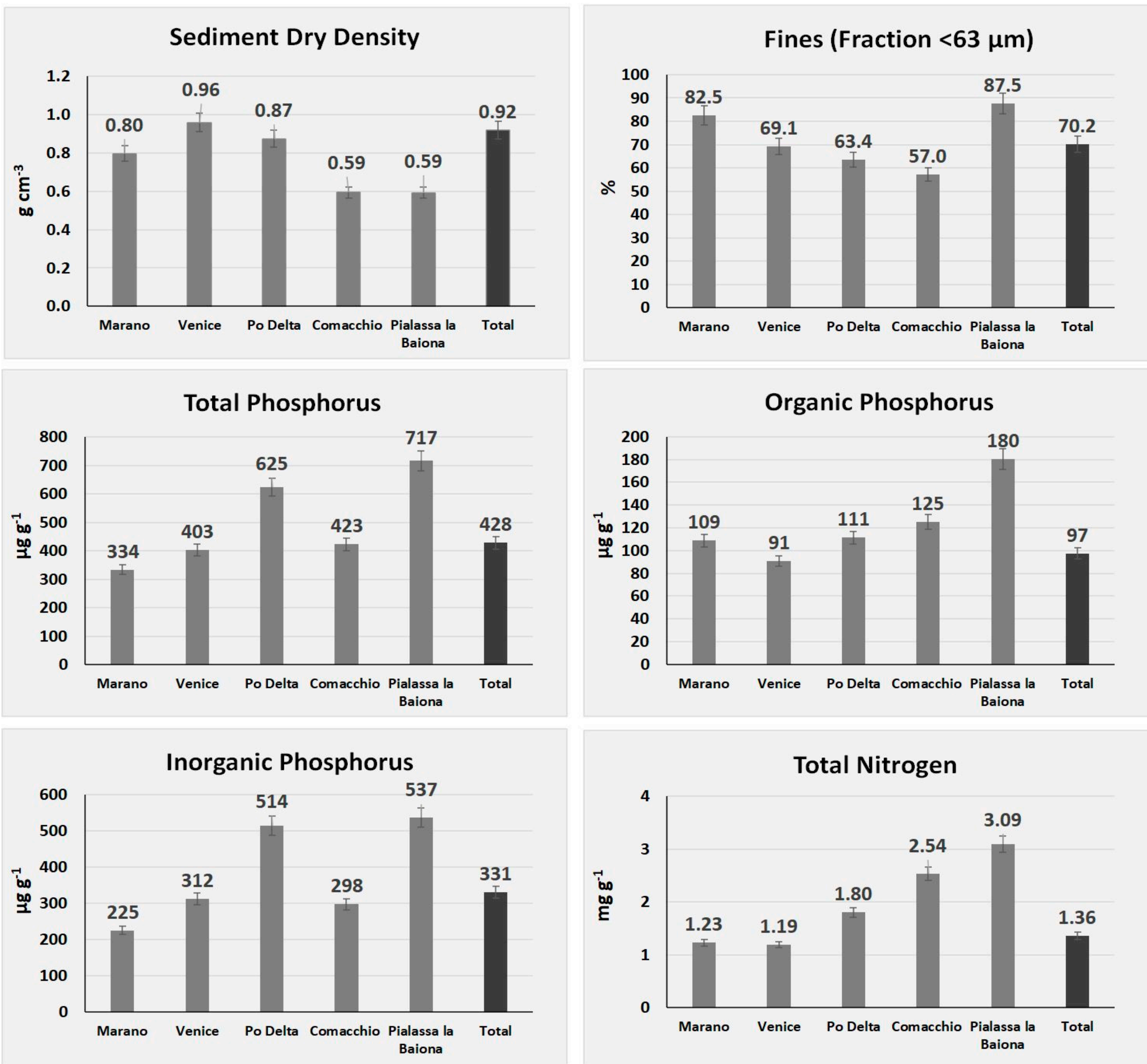

Figure 2. Average values of sediment dry density (g cm^{-3}), fines (fraction < 63 µm), phosphorus species (P_{tot}, P_{inorg}, P_{org}) and total nitrogen (N_{tot}) in the studied TWSs.

On the whole, the average dry density of all the sampling sites was 0.92 g cm^{-3} on a dry weight (dwt) basis. The highest density was recorded in the Venice lagoon (0.96 g dwt cm^{-3}), whereas Pialassa della Baiona and the Comacchio valleys showed the lowest values (0.59 g cm^{-3}). The amount of fines on average was 70.2%, with the highest and the lowest concentrations in the Pialassa della Baiona (87.5%) and Comacchio valleys, (57.0%), respectively. Pialassa della Baiona also showed the highest concentrations of N_{tot} (3.09 mg g^{-1}), P_{tot} (717 µg g^{-1}), P_{inorg} (537 µg g^{-1}) and P_{org} (180 µg g^{-1}). Total phosphorus showed the lowest value at Marano (334 µg g^{-1}), where N_{tot} was also particularly low (1.23 mg g^{-1}), just higher than that found in the Venice lagoon (1.19 mg g^{-1}).

3.2. Nutrient Variations in the Venice Lagoon

The nutrient concentrations recorded in the whole Venice lagoon by our research team were recorded during four surveys carried out in late spring to early summer 2003, 2011, 2014 and 2018 (Table 1).

Table 1. Changes of total nutrient concentrations in surface sediments of the Venice lagoon.

Phosphorus and Nitrogen Changes in the Whole Venice Lagoon													
2003–2018													
Years	Sediment Thickness	Stations	Total Phosphorus µg g^{-1}					Total Nitrogen mg g^{-1}					
	cm	N°	Mean		Std	min	max	Mean		STD	min	max
2003	5	165	409	±	113	201	677	1.42	±	1.42	0.09	12.9
2011	5	118	403	±	113	199	684	1.19	±	1.95	0.03	11.5
2014	5	88	412	±	111	212	707	1.38	±	1.30	0.17	6.98
2018	5	88	403	±	116	180	716	1.28	±	1.09	0.19	6.98

Both P_{tot} and N_{tot} showed no significant changes. Indeed, the mean values of P_{tot} recorded in this period were almost the same, ranging from 403 to 412 µg g^{-1}. Similar results were recorded for the minimum and maximum values. On the other hand, N_{tot} showed more marked changes. The mean concentration recorded in 2003 was 1.42 mg g^{-1}. This value decreased to 1.19 mg g^{-1} in 2011 and increased again in 2014 (1.38 mg g^{-1}) and 2018 (1.28 mg g^{-1}). The minimum and maximum values were also different, showing more marked extreme values in 2003 and 2011, compared to subsequent periods.

All data for the N_{tot}, P_{tot} and P_{org} concentrations recorded in the surface sediments of the whole Venice lagoon were plotted on maps within six concentration ranges (Figure 3). In 2003, N_{tot} showed the highest concentrations in the south, southwestern and northern parts of the lagoon. The same was also observed in 2014 and 2018. On the other hand, in 2011, N_{tot} showed a marked decreased in the whole lagoon, with the lowest values in the central basin.

Total phosphorus did not show significant changes but only a spatial redistribution with the highest concentrations found in the same areas of N_{tot}. Organic phosphorus showed greater changes. Indeed, the mean concentration recorded in 2003 was 79 ± 56 µg g^{-1}. This value increased to 91 ± 63 µg g^{-1} in 2011, only to decrease to 81 ± 54 µg g^{-1} in 2018. The highest changes were recorded in the eastern parts of the central and southern basins.

A better interpretation of the nutrient trends can be obtained from the temporal changes that occurred in the central lagoon, which was monitored several times by our research group between 1987 and 2018, sampling the same 34 stations and considering the same sediment thickness (Table 2).

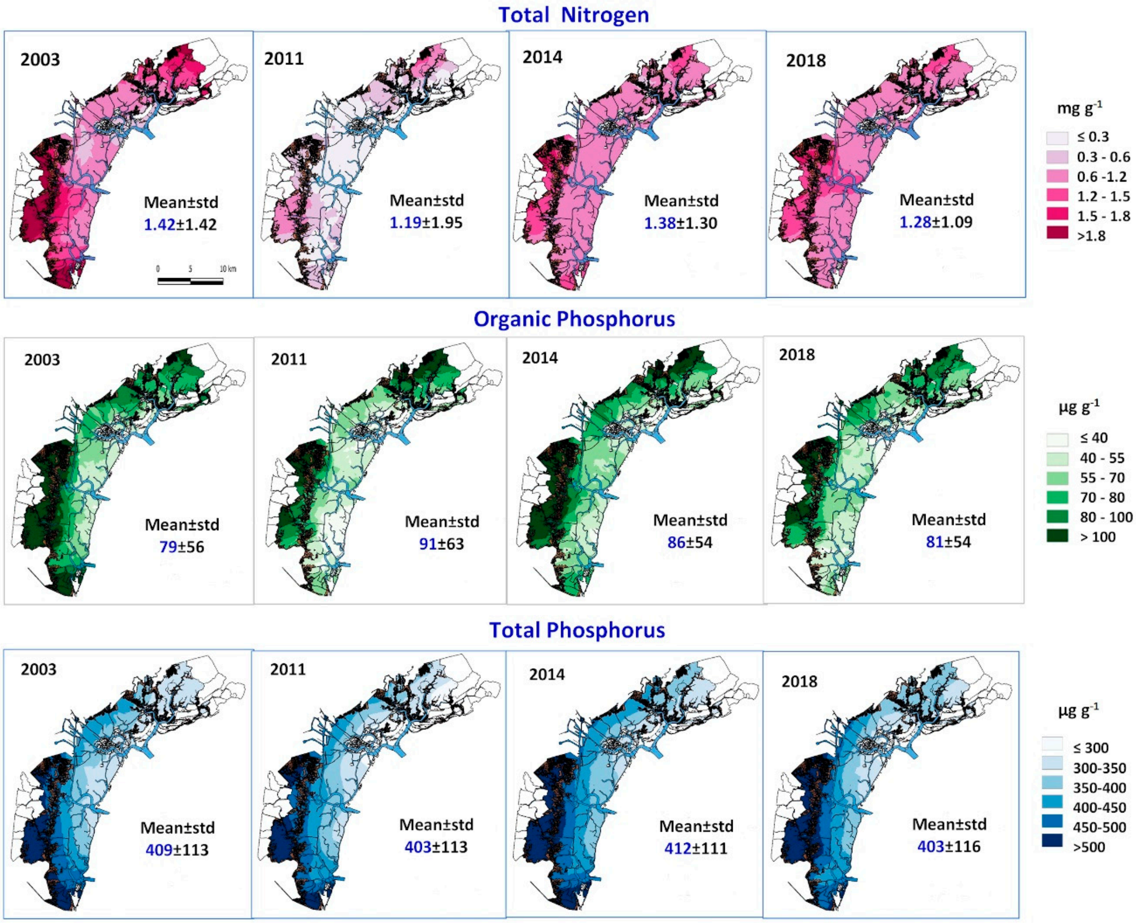

Figure 3. Distribution maps of N_{tot}, P_{org} and P_{tot} in the surface sediments of the whole Venice lagoon.

Table 2. Changes of total nutrient concentrations in surface sediments of the central basin of the Venice lagoon.

Total Nitrogen (Central lagoon)							
	1987	1993	1998	2003	2011	2014	2018
	mg/g						
Stations N°	34	34	34	34	35	34	34
Mean	1.25	1.26	0.89	0.71	0.34	0.83	0.81
Std	0.59	0.70	0.38	0.36	0.52	0.47	0.45
Min	0.16	0.25	0.13	0.09	0.03	0.17	0.22
Max	2.72	2.85	1.45	1.48	2.07	2.02	2.37

Inorganic Phosphorus (Central lagoon)							
	1987	1993	1998	2003	2011	2014	2018
	µg/g						
Stations N°	34	34	34	34	35	34	34
Mean	287	301	308	305	283	309	293
Std	53	66	53	76	62	62	65
Min	193	185	202	199	179	179	164
Max	423	461	430	485	454	424	467

Total Phosphorus (Central lagoon)							
	1987	1993	1998	2003	2011	2014	2018
	mg/g						
Stations N°	34	34	34	34	34	34	34
Mean	397	372	370	358	341	375	357
Std	82	86	79	99	84	85	86
Min	240	236	221	201	199	212	180
Max	577	597	560	635	563	547	548

Organic Phosphorus (Central lagoon)							
	1987	1993	1998	2003	2011	2014	2018
	µg/g						
Stations N°	34	34	34	34	34	34	34
Mean	109	71	62	53	58	66	64
Std	47	34	41	35	34	33	35
Min	45	22	12	2	10	20	10
Max	240	149	195	150	149	143	166

The total nitrogen displayed the greatest changes. In late spring to early summer 1987, during the period of luxuriant macroalgal growth, the mean N_{tot} value was 1.25 mg g^{-1}

(Table 2, Figure 4). The mean value in the period of clam harvesting decreased to 0.34 mg g^{-1} in late spring to early summer 2011, then increased slightly in 2014 and 2018 (0.83 and 0.81 mg g^{-1}, respectively). The decrease in the period 1987–2011 was −72.8%, whereas between 1987 and 2018 it was −35.2% (Figure 4).

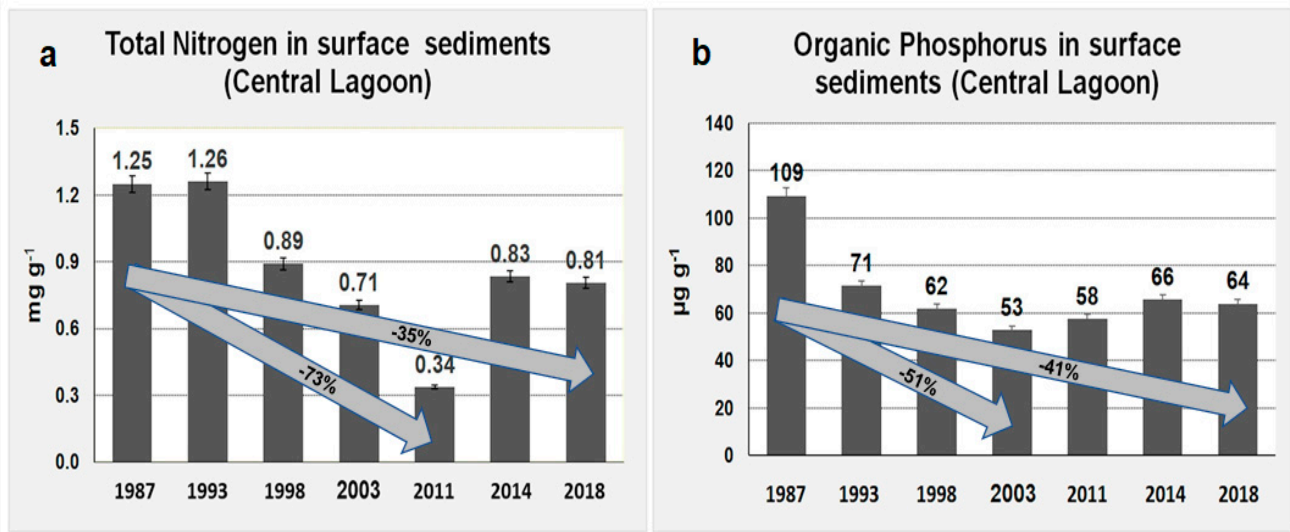

Figure 4. Average values of (**a**) N_{tot} and (**b**) P_{org} concentrations recorded in the surface sediments (34 stations) and in the central Venice lagoon during different periods. Arrows show the concentrations decreased after 1987, with the lowest values recorded in 2011 for N_{tot} and 2003 for P_{org}, before the values increase to those recorded in 2018.

The total phosphorus and P_{inorg} showed no significant changes (Table 2). Instead, P_{org} had similar variations to N_{tot}. Indeed, P_{org} decreased from 109 µg g^{-1} in 1987 to 53 µg g^{-1} in 2003, and increased to 66 and 64 µg g^{-1} in 2014 and 2018, respectively. The difference between 1987 and 2003 was −51.4%, whereas between 1987 and 2018 it was −41.3% (Figure 4).

The one-way ANOVA of the N_{tot} and P_{org} concentrations in surface sediments of the central Venice lagoon between the successive sampling periods showed a different behavior for the two nutrients (Table 3). Nitrogen decrease occurred between 1993 and 2011 and was significantly related to clam harvesting activities. In contrast, P_{org} changes were only significant in the period 1987–1993 when the macroalgal biomass of nuisance macroalgae decreased sharply.

3.3. Statistical Analyses

The statistical analysis (non-parametric Spearman's coefficients) of nutrient concentrations and sediment characteristics recorded in all the considered TWSs showed a high number of positive or inverse correlations between the sediment dry density and grain-size (fines) and the nutrient concentrations (Table 4). Among them, particularly relevant was the negative correlation of sediment density with P_{org} ($r = -0.84$). Conversely, P_{inorg} showed the fewest number of correlations with the other parameters.

Principal component analyses (PCAs) of the first two components applied to the whole stations sampled in the Marano-Grado lagoons in 2007, Po Delta lagoons and ponds in 2008, Comacchio valleys and Pialassa della Baiona in 2009 and 2011 (the closest dates to those sampled in the Venice lagoon) are shown in Figure 5a. The first two components explained 70.8% of the total variance and dry density. Organic phosphorus and P_{inorg} showed a loading > 0.7. In addition, PCA highlighted the affinity among parameters, showing a strong association of nutrients with fines as opposed to the sediment density.

Table 3. One-way ANOVA values between the different sampling periods of N_{tot} and P_{org} in surface sediments of the central Venice lagoon. n.s. = not significant values.

Total Nitrogen (one-way ANOVA 34 stations)		
Period	Significance	Scenario
1987–1993	n.s.	Macroalgal biomass decrease
1993–1998	$p < 8.47 \times 10^{-3}$	Clam harvesting
1998–2003	$p < 4.27 \times 10^{-2}$	
2003–2011	$p < 7.81 \times 10^{-4}$	
2011–2014	$p < 8.68 \times 10^{-5}$	Lagoon resilience
2014–2018	n.s.	
1987–2018	$p < 6.97 \times 10^{-4}$	Total
Organic Phosphorus (one-way ANOVA 34 stations)		
Period	Significance	Scenario
1987–1993	$p < 2.86 \times 10^{-4}$	Macroalgal biomass decrease
1993–1998	n.s.	Clam harvesting
1998–2003	n.s.	
2003–2011	n.s.	
2011–2014	n.s.	Lagoon resilience
2014–2018	n.s.	
1987–2018	$p < 2.53 \times 10^{-5}$	Total

Table 4. Spearman's non-parametric coefficients between phosphorus species, total nitrogen, fines and density of surface sediments of all the lagoons and ponds considered. In blue are significant values: $p < 0.05$ for $r \geq \pm 0.19$; in red are highly significant values $p < 0.001$ for $r \geq \pm 0.41$.

Spearman's Non Parametric Coefficients						
	Fines	Density	P_{tot}	P_{inorg}	P_{org}	N_{tot}
Fines	1.00					
Density	−0.55	1.00				
P_{tot}	0.22	−0.50	1.00			
P_{inorg}	0.08	−0.14	0.85	1.00		
P_{org}	0.49	−0.84	0.57	0.13	1.00	
N_{tot}	0.19	−0.46	0.41	0.20	0.51	1.00

The PCA of the transposed matrix applied to the same parameters and stations (Figure 5b) shows the clustering among the stations of the different TWSs. The stations of the Venice lagoon cover the whole biplot, showing high heterogeneity. Among them, some outliers are represented by stations placed inside choked fishing ponds (Doga valley, Cavallino valley) that present peculiar conditions, being separated from the tidal exchange of the open lagoon. The other lagoons and ponds are grouped and placed only in a restricted part of the biplot, showing greater homogeneity.

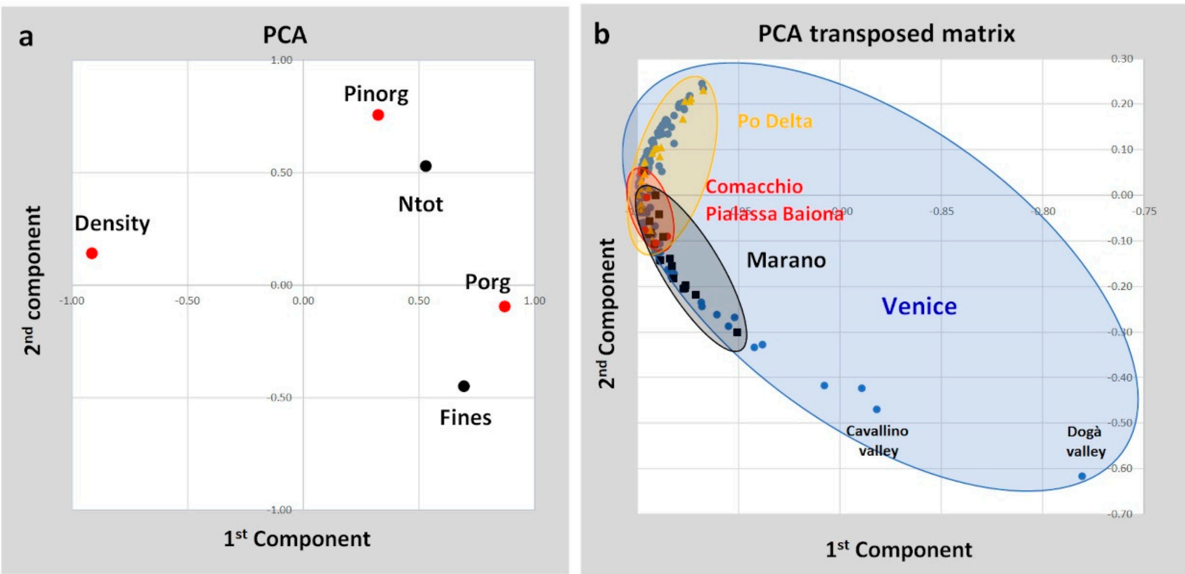

Figure 5. (**a**) PCA among nutrient species, sediment density and grain size (fines). Red circles represent values of loading > 0.7. (**b**) PCA of the transposed matrix to highlight the station and lagoon associations. The different colors show different TWSs. Blue circles: Venice lagoon; black squares: Marano-Grado lagoon; ocher triangles: Po Delta lagoons and ponds; in red: Comacchio valleys and Pialassa della Baiona.

4. Discussion

The concentrations of nutrients in the surface sediments of the lagoons of the north-western Adriatic Sea showed a close relationship with sediment characteristics such as the grain size and density. In fact, finer-sized sediments had a greater relative surface and a greater capacity to retain nutrients and pollutants. Vaze and Chew [52] found that almost all the TP and TN were attached to sediments with grain sizes between 11 and 150 µm. Furthermore, their density was lower due to the presence of a greater quantity of interstitial water, which in turn contains, high concentrations of nutrients, especially ammonium [53].

In the case of the Venice lagoon, of which we have numerous data collected in different periods, significant temporal variations due to different anthropogenic impacts were also monitored.

In general, the highest sediment concentrations of N_{tot}, P_{tot}, P_{inorg} and P_{org} were recorded in Pialassa della Baiona, characterized by the highest percentage of fines (fraction < 63 µm: 87.5%) and the lowest density (0.59 g dwt cm^{-3}). The same low sediment density was also recorded in the Comacchio valleys. However, the Comacchio valleys showed a significantly lower percentage of fines (57.0%), which could explain the lower concentrations of nitrogen and phosphorus in the sediments of this basin. Moreover, the poor water renewal of the Comacchio valleys accounted for the bad ecological conditions of these large ponds recorded since the last two decades of the 20th century. Despite the fact that for this basin, previous data on nutrient concentrations are missing, the list of macrophytes reported by [54] and [55] highlights that before the 1970s, the Comacchio valleys were colonized by aquatic angiosperms such as *Ruppia cirrhosa* (Petagna) Grande and *Zostera noltei* Hornemann, and sensitive macroalgae. First of all, these included *Lamprothamnium papulosum* (Wallroth) J. Grove, a Chlorophycea even more sensitive than aquatic angiosperms and currently present only in some fishing valleys of the Venetian lagoon such as the Cavallino valley, which shows almost pristine ecological conditions [43]. The presence of that vegetation was linked to a low trophy and nutrient concentrations certainly lower than the current ones. Indeed, in the following years, almost all the macrophytes disappeared from the valleys and only cyanobacteria and phytoplankton were recorded [44–46]. Discharges from fish farms, especially from eel breeding, the polluted water drainage from extensive agricultural practices and freshwater inputs from the Reno river have irremediably changed the trophic status of these basins and eliminated the macrophytes present, even those of low ecological value. Recently, some small thalli of some tionitrophilic Chlorophyceae, mostly Ulvaceae, have been recorded at only 5–15 cm from the surface because the waters were very turbid and the transparency never exceeded 25–40 cm all year round.

On the whole, the Marano-Grado and Venice lagoons were the less eutrophicated basins, showing the lowest mean concentrations of P_{tot} (334 and 403 μg g^{-1}, respectively) and N_{tot} (1.23 and 1.19 mg g^{-1}, respectively). The Comacchio valleys had intermediate concentrations.

However, for the Venice lagoon, many data are available from the mid-20th century (Table 5).

Table 5. Global changes of total nutrient concentrations in surface sediments of the Venice lagoon since the mid-20th century.

Phosphorus and Nitrogen Changes in the Whole Lagoon													
1948–2018													
Authors	Year	Sediment thickness cm	Stations N°	Total Phosphorus μg g^{-1} Mean		Std	Min	Max	Total Nitrogen mg g^{-1} Mean		Std	Min	Max
Perin, 1974 [49]	1948–1949	30	-	24	±	16	-	50	1.00	±	0.86	-	1.96
Perin, 1974 [49]	1968–1973	30	-	164	±	79	-	250	1.86	±	2.20	-	3.56
Perin et al., 1983 [50]	1983	20	-	454	±	126	-	682	1.33	±	0.59	-	2.74
CVN, MAV, 1990 [27]	1987–1988	20	-	339	±	215	-	1102	1.33	±	0.89	-	4.80
This paper	2003	5	165	409	±	113	201	677	1.42	±	1.42	0.09	12.9
	2011	5	118	403	±	113	199	684	1.19	±	1.95	0.03	11.5
	2014	5	88	412	±	111	212	707	1.38	±	1.30	0.17	6.98
	2018	5	88	403	±	116	180	716	1.28	±	1.09	0.19	6.98

The concentrations of P_{tot} and N_{tot} recorded in 1948–49, before the development of the industrial area of Porto Marghera, were very low and can be considered the background values for the lagoon. Indeed, the mean value of the P_{tot} concentration was only 24 μg g^{-1}, whereas N_{tot} was 1.00 mg g^{-1} [49]. Twenty years later, both nutrients were recorded by the same authors at the same stations to have increased markedly. Total phosphorus increased ca. 6.8 times (164 μg g^{-1}) and N_{tot} almost doubled (1.86 mg g^{-1} [49]). The highest P_{tot} concentrations were recorded in 1983, with a mean value of 454 μg g^{-1} [50], ca. 19 times greater than the value recorded in 1948–49, whereas N_{tot} reached the highest value in 1968–73, with a mean value of 1.86 mg g^{-1} [49]. However, single stations close to the industrial area of Porto Marghera reached 1102 μg g^{-1} for P_{tot} in 1987–88 and 4.9 mg g^{-1} for N_{tot} in 2003. Indeed, after the Second World War, the lagoon received sewage effluents from about 300,000 inhabitants of Venice, Mestre, Marghera and Chioggia, wastes from chemical and steel plants located in the 30-km^2 Porto Marghera industrial area and runoff from an intensively-cultivated drainage basin (ca. 2000 km^2). Particularly relevant was the massive extraction of phosphorus from phosphorites and the industrial synthesis of ammonia to support the rapidly expanding agricultural production [56,57]. The main consequence was the high pollution of water and sediments. Phosphorus rapidly accumulated in surface sediments until the end of production in the mid-1980s. In the following years, P_{tot} showed a reverse trend but its concentrations fluctuated between 403 and 412 μg g^{-1} because this element remained trapped in the sediments due to its sedimentary cycle. In contrast, N_{tot} changed slightly. It was higher in 2003 (1.42 ± 1.42 mg g^{-1}) and decreased markedly in 2011 (1.19 ± 1.95 mg g^{-1}) during the maximum clam fishing activities [2] that favored nitrogen release in the water column as ammonium and loss into the atmosphere due to the high denitrification processes [58]. In the following years, when clam fishing activities were negligible, N_{tot} increase again.

The studies carried out in the central part of the Venice lagoon are more recent but they show the variations of nutrients in the sediments (Table 2, Figure 4) during the various scenarios that have characterized the lagoon from the 1980s to today. In addition, for the central lagoon, P_{inorg} and P_{org} were also determined, highlighting the significant changes of P_{org} while P_{inorg} remained almost unchanged. The concentrations of P_{org} and N_{tot} were mainly affected by the presence of a high biomasses of macroalgae and the intensity of clam-fishing activities, which had an inverse impact on nutrient concentrations. Macroalgae produced great quantities of decomposing organic matter, which enriched surface sediments with both N_{tot} and P_{org}, whereas biomass reduction and fishing activities occurring between 1995 and 2012, plowing the sediments to a depth of 15–20 cm, which released into the water column the ammonium and reactive phosphorus present in interstitial waters. As a consequence, the N_{tot} (−73%) in 2011 and P_{org} (−51%) in 2003 reached their minimum concentrations (Figure 4). In the following years, when clam fishing was negligible or completely absent, both N_{tot} and P_{org} increased again but without reaching the concentrations recorded in 1987 due to the negligible macroalgal biomass present in this period. A one-way ANOVA confirmed that the most significant decrease of N_{tot} was due to clam-harvesting that triggered the release of ammonium from surface sediments into the water column. In contrast, the strong reduction of the macroalgal biomass [36] was the main cause of P_{org} decreasing. The analysis of the global data (Spearman's coefficients and PCA) confirms that nutrient concentrations were positively correlated with the sediment grain size (fines) and inversely with sediment density as recorded from many other analyses carried out in these environments [24,59].

Finally, plotting all the stations in the transposed PCA matrix highlights that the concentrations of nutrients in the surface sediments of the Venice lagoon cover all the concentrations recorded in the Po Delta, Marano-Grado, Comacchio and Pialassa della Baiona, which present lower environmental variability, as recorded in [24].

If we consider the concentrations of nutrients in the sediments of other lagoons recorded in the literature, Sørensen et al. [60] reported the concentrations of N_{tot} and P_{tot} in the Keta lagoon (Ghana) and compared their results with those of other lagoons around the world. In the Keta lagoon, P_{tot} and N_{tot} were in the ranges of 130–240 μg g^{-1} and 0.1–1.0 mg g^{-1}, respectively. These values were similar to the values recorded in a lagoon of the Balearic islands, Spain [61] and in the Ringkjøbing Fjord, Denmark [62] (Table S2, Supplementary Material), but were significantly lower than the values recorded in this study.

Nutrient concentrations similar to those recorded in the TWS of the northwestern Adriatic Sea were recorded in a system of eutrophic lagoons in northwestern Mexico [63], where P_{tot} and N_{tot} were in the ranges of 341–1240 μg g^{-1} and 0.15–8.89 mg g^{-1}, respectively. High nutrient values were also recorded in the Méjean-Pérols lagoon (France) [64], with P_{tot} and N_{tot} concentrations in the ranges of 398–1147 μg g^{-1} and 1.9–6.0 mg g^{-1}, respectively. Intermediate concentrations were found in some lagoons of the Sabana-Camagüey archipelago at Cuba [65]. In these basins, P_{tot} and N_{tot} showed concentrations up to 241 μg g^{-1} and 11.5 mg g^{-1}, respectively. Therefore, the TWSs of the northwestern Adriatic Sea are placed among the most eutrophic basins and have concentrations strongly linked to the grain-size of the sediment. The Venice lagoon, due to its large surface and the heterogeneity of its micro-environments, presents conditions that cover the concentrations found in most of the other basins.

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References

1. Solidoro, C.; Bandelj, V.; Bernardi, F.A.; Camatti, E.; Ciavatta, S.; Cossarini, G.; Facca, C.; Franzoi, P.; Libralato, S.; Melaku Canu, D.; et al. Response of the Venice Lagoon Ecosystem to Natural and Anthropogenic Pressures over the last 50 years. In *Coastal Lagoons—Critical Habitats of Environmental Change*; Kennish, M.J., Paerl, H.W., Eds.; CRC Press: Boca Raton, FL, USA, 2010; Chapter 19; pp. 483–511.
2. Sfriso, A.; Buosi, A.; Mistri, M.; Munari, C.; Franzoi, P.; Sfriso, A.A. Long-Term Changes of the Trophic Status in Transitional Ecosystems of the Northern Adriatic Sea, Key Parameters and Future Expectations: The Lagoon of Venice as a Study Case. *Nat. Conserv.* **2019**, *34*, 193–215. [CrossRef]
3. Jessen, C.; Bednarz, V.N.; Rix, L.; Teichberg, M.; Wild, C. Marine Eutrophication. In *Environmental Indicators*; Armon, R.H., Hänninen, O., Eds.; Springer: Berlin, Germany, 2015; pp. 177–203.
4. Wolfe, D.A. *Estuarine Variability*; Academic Press, Inc: Orlando, FL, USA, 1986; p. 509.
5. Schramm, W.; Nienhuis, P.H. *Marine Benthic Vegetation. Recent Changes and Effects of Eutrophication*; Springer: Berlin, Germany, 1990; p. 470.
6. Nedwell, D.B.; Jickells, T.D.; Trimmer, M.; Sanders, R. Nutrients in Estuaries. *Estuaries* **1999**, *29*, 43–92.
7. Pastres, R.; Solidoro, C.; Ciavatta, S.; Petrizzo, A.; Cossarini, G. Long-term changes of inorganic nutrients in the Lagoon of Venice (Italy). *J. Mar. Syst.* **2004**, *51*, 179–189. [CrossRef]
8. Velasco, J.; Lloret, J.; Millan, A.; Marin, A.; Barahona, J.; Abellan, P.; Sanchez-Fernandez, D. Nutrient and particulate inputs into the mar menor lagoon (Se Spain) from an intensive agricultural watershed. *Water Air Soil Pollut.* **2006**, *176*, 37–56. [CrossRef]
9. Moutin, T.; Raimbault, P.; Golterman, H.L.; Coste, B.; Rouzic, B. The input of nutrients by the Rhône river into the Mediterranean Sea: Recent observations and comparison with earlier data. *Hydrobiologia* **1997**, *373*, 237–246. [CrossRef]
10. Brown, J.B.; Sprague, L.A.; DuPree, J.A. Nutrient sources and transport in the Missouri River basin, with emphasis on the effects of irrigation and reservoirs1. *JAWRA J. Am. Water Resour. Assoc.* **2011**, *47*, 1034–1060. [CrossRef]
11. Collavini, F.; Bettiol, C.; Zaggia, L.; Zonta, R. Pollutant loads from the drainage basin to the Venice Lagoon (Italy). *Environ. Int.* **2005**, *31*, 939–947. [CrossRef] [PubMed]
12. Bartoli, M.; Nizzoli, D.; Viaroli, P.; Turolla, E.; Castaldelli, G.; Fano, E.A.; Rossi, R. Impact of Tapes philippinarum farming on nutrient dynamics and benthic respiration in the Sacca di Goro. *Hydrobiologia* **2001**, *455*, 203–212. [CrossRef]
13. Castaldelli, G.; Mantovani, S.; Welsh, D.T.; Rossi, R.; Mistri, M.; Fano, E.A. Impact of commercial clam harvesting on water column and sediment physicochemical characteristics and macrobenthic community structure in a lagoon (Sacca di Goro) of the Po River Delta. *Chem. Ecol.* **2003**, *19*, 161–171. [CrossRef]
14. Pranovi, F.; Da Ponte, F.; Torricelli, P. Historical changes in the structure and functioning of the benthic community in the lagoon of Venice. *Estuar. Coast. Shelf Sci. USA* **2008**, *76*, 753–764. [CrossRef]
15. Sfriso, A.; Facca, C.; Ceoldo, S.; Silvestri, S.; Ghetti, P.F. Role of macroalgal biomass and clam fishing on spatial and temporal changes in N and P sedimentary pools in the central part of the Venice lagoon. *Oceanol. Acta* **2003**, *26*, 3–13. [CrossRef]
16. Sfriso, A.; Facca, C.; Marcomini, A. Sedimentation rates and erosion processes in the lagoon of Venice. *Environ. Int.* **2005**, *31*, 983–992. [CrossRef] [PubMed]
17. Cunha, D.G.F.; Calijuri, M.D.C.; Dodds, W.K. Trends in nutrient and sediment retention in great plains reservoirs (USA). *Environ. Monit. Assess.* **2014**, *186*, 1143–1155. [CrossRef] [PubMed]
18. Sfriso, A.; Pavoni, B.; Marcomini, A.; Orio, A.A. Annual variations of nutrients in the lagoon of Venice. *Mar. Pollut. Bull.* **1988**, *19*, 54–60. [CrossRef]
19. Song, Y.; Zhou, Q.; Song, X.; Zhang, W.; Sun, T. Accumulation of pollutants in sediments and their eco-toxicity in the wastewater irrigation channel of western Shenyang. *Ying yong sheng tai xue bao = J. Appl. Ecol.* **2004**, *15*, 1926–1930.
20. Sakan, S.M.; Đorđević, D.S.; Manojlović, D.D.; Predrag, P. Assessment of heavy metal pollutants accumulation in the Tisza river sediments. *J. Environ. Manag.* **2009**, *90*, 3382–3390. [CrossRef] [PubMed]
21. Marcomini, A.; Sfriso, A.; Zanette, M. Macroalgal Blooms, Nutrient and Trace Metal Cycles in a Coastal Lagoon. In *Macroalgae, Eutrophication and Trace Metal Cycling in Estuaries and Lagoons*; Rijstenbil, J.W., Haritonidis, S., Eds.; Proceedings of the COST-48 Symposium of Sub Group III Thessaloniki, Commission of the European Communities, Biotechnology Research for Innovation, Development and Growth in Europe (BRIDGE); Thessaloniki, Greece, 24–26 September 1993, pp. 66–90.
22. Clavier, J.; Chardy, P.; Chevillon, C. Sedimentation of particulate matter in the south-west lagoon of New Caledonia: Spatial and temporal patterns. *Estuar. Coast. Shelf Sci.* **1995**, *40*, 281–294. [CrossRef]
23. Sfriso, A.; Pavoni, B.; Marcomini, A.; Raccanelli, S.; Orio, A. Particulate matter deposition and nutrient fluxes onto the sediments of the venice lagoon. *Environ. Technol.* **1992**, *13*, 473–483. [CrossRef]

24. Sfriso, A.A.; Buosi, A.; Facca, C.; Sfriso, A.A. Role of environmental factors in affecting macrophyte dominance in transitional environments: The Italian Lagoons as a study case. *Mar. Ecol.* **2017**, *105*, 13. [CrossRef]
25. Giordani-Soika, A.; Perin, G. L'inquinamento della laguna di Venezia: Studio delle modificazioni chimiche e del popolamento sottobasale dei sedimenti lagunari negli ultimi vent'anni. *Boll. Mus. Civico Storia Nat. Venezia.* **1974**, *26*, 25–68.
26. Cossu, A.; De Fraja-Frangipane, E. *Stato delle conoscenze sullo inquinamento della laguna di Venezia*; Progetto Venezia, Ministero dei Lavori Pubblici, Magistrato alle Acque, Consorzio Venezia Nuova: Venezia, Italy, 1985; 4 vol.
27. Consorzio Venezia Nuova (CVN); Magistrato alle Acque (MAV). *Nuovi Interventi per la Salvaguardia di Venezia*; Rapporto sullo Stato Attuale dell'Ecosistema Lagunare. Studio 1.3.9: Final Report: Venice, Italy, 1990; p. 361.
28. Pavoni, B.; Sfriso, A.; Donazzolo, R.; Orio, A.A. Influence of waste waters from the city of Venice and the hinterland on the eutrophication of the lagoon. *Sci. Total. Environ.* **1990**, *96*, 235–252. [CrossRef]
29. Marcomini, A.; Sfriso, A.; Pavoni, B.; Orio, A.A. Eutrophication of the Lagoon of Venice: Nutrient Loads and Exchanges. In *Eutrophic Shallow Estuaries and Lagoons*; Mc Comb, A.J., Ed.; CRC Press: Boca Raton, FL, USA, 1995; pp. 59–80.
30. Sfriso, A.; Marcomini, A. The Lagoon of Venice (Italy). In *Marine Benthic Vegetation, Ecological Studies*; Schramm, W., Nienhuis, P.N., Eds.; Springer Verlag: Berlin/Heidelberg, Germany, 1996.
31. Sfriso, A.; Facca, C.; Ceoldo, S.; Marcomini, A. Recording the occurrence of trophic level changes in the lagoon of Venice over the '90s. *Environ. Int.* **2005**, *31*, 993–1001. [CrossRef]
32. Falace, A.; Curiel, D.; Sfriso, A. Study of the macrophyte assemblages and application of phytobenthic indices to assess the Ecological Status of the Marano-Grado Lagoon (Italy). *Mar. Ecol.* **2009**, *30*, 480–494. [CrossRef]
33. Sfriso, A.; Facca, C.; Bon, D.; Giovannone, F.; Buosi, A. Using phytoplankton and macrophytes to assess the trophic and eco-logical status of some Italian transitional systems. *Cont. Shelf Res.* **2014**, *81*, 88–98. [CrossRef]
34. Sfriso, A.; Facca, C. Distribution and production of macrophytes in the lagoon of Venice. Comparison of actual and past abundance. *Hydrobiologia* **2007**, *577*, 71–85. [CrossRef]
35. Gačić, M.; Mosquera, I.M.; Kovačević, V.; Mazzoldi, A.; Cardin, V.; Arena, F.; Gelsi, G. Temporal variations of water flow between the Venetian lagoon and the open sea. *J. Mar. Syst.* **2004**, *51*, 33–47. [CrossRef]
36. Masiol, M.; Facca, C.; Visin, F.; Sfriso, A.; Pavoni, B. Interannual heavy element and nutrient concentration trends in the top sediments of Venice Lagoon (Italy). *Mar. Pollut. Bull.* **2014**, *89*, 49–58. [CrossRef] [PubMed]
37. Zuliani, A.; Zaggia, L.; Collavini, F.; Zonta, R. Freshwater discharge from the drainage basin to the Venice Lagoon (Italy). *Environ. Int.* **2005**, *31*, 929–938. [CrossRef]
38. Cucco, A.; Umgiesser, G. Modeling the Venice Lagoon residence time. *Ecol. Model.* **2006**, *193*, 34–51. [CrossRef]
39. Sfriso, A.; Marcomini, A. Decline of Ulva growth in the lagoon of Venice. *Bioresour. Technol.* **1996**, *58*, 299–307. [CrossRef]
40. Gatto, F.; Marocco, R. Morfometria e geometria idraulica dei canali della laguna di Grado (Friuli-Venezia Giulia). *Geogr. Fis. e Din.* **1993**, *16*, 107–120.
41. Marocco, R. Sediment distribution and dispersal in northern Adriatic lagoons (Marano and Grado paralic system). *Geologia, serie 3a* **1995**, *57*, 77–89.
42. Falace, A.; Sfriso, A.; Curiel, D.; Matassi, G.; Aleffi, I.F. The Marano and Grado lagoon (North Adriatic Sea). In *Flora and Vegetation of the Italian Transitional Water Systems*; Cecere, E., Petrocelli, A., Izzo, G., Sfriso, A., Eds.; CoRiLa, Multigraf: Spinea, Italy, 2009; pp. 1–16.
43. Sfriso, A.; Facca, C.; Bon, D.; Buosi, A. Macrophytes and ecological status assessment in the Po delta transitional systems, Adriatic Sea (Italy). Application of Macrophyte Quality Index (MaQI). *Acta Adriat.* **2016**, *57*, 209–226.
44. Sorokin, Y.; Gnes, A. Structure and functioning of the anthropogenically transformed Comacchio lagoonal ecosystem (Ferrara, Italy). *Mar. Ecol. Prog. Ser.* **1996**, *133*, 57–71. [CrossRef]
45. Sorokin, Y.I.; Zakuskina, O.Y. Features of the comacchio ecosystem transformed during persistent bloom of picocyano-bacteria. *J. Oceanogr.* **2010**, *66*, 373–387. [CrossRef]
46. Munari, C.; Mistri, M. Ecological status assessment and response of benthic communities to environmental variability: The Valli di Comacchio (Italy) as a study case. *Mar. Environ. Res.* **2012**, *81*, 53–61. [CrossRef]
47. Sfriso, A.; Buosi, A.; Wolf, M.A.; Sfriso, A.A. Invasion of alien macroalgae in the Venice Lagoon, a pest or a resource? *Aquat. Invasions* **2020**, *15*, 245–270. [CrossRef]
48. Covelli, S.; Emili, A.; Acquavita, A.; Koron, N.; Fraganeli, J. Benthic biogeo-chemical cycling of mercury in two contaminated northern Adriatic coastal lagoons. *Cont. Shelf Res.* **2011**, *31*, 1777–1789. [CrossRef]
49. Perin, G. L'inquinamento della Laguna di Venezia: Sintesi di sette anni di ricerche. *Convegno: Tavola Rotonda "Problemi dell'inquinamento lagunare"* **1974**, *1*, 47–89.
50. Perin, G.; Pastre, B.; Orio, A.A.; Carniel, A.; Gabelli, A.; Pavoni, B.; Donazzolo, R.; Pasquetto, A. Inquinamento chimico del-la laguna di Venezia: Nutrienti e metalli pesanti nei sedimenti. *Acqua Aria* **1983**, *6*, 623–632.
51. Aspila, K.I.; Agemian, H.; Chau, A.S.Y. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. *Analyst* **1976**, *101*, 187–197. [CrossRef]
52. Vaze, J.; Chew, F.H.S. Nutrient loads associated with different sediment sizes in urban stormwater and surface pollutants. *J. Environ. Eng.* **2004**, *130*, 391–396. [CrossRef]
53. Sfriso, A.; Marcomini, A. Macrophyte production in a shallow coastal lagoon. Part I. Coupling with physico-chemical param-eters and nutrient concentrations in waters. *Mar. Environ. Res.* **1997**, *44*, 351–375. [CrossRef]

54. Ferrari, C.; Pirola, A.; Piccoli, F. Carta della vegetazione delle Valli di Comacchio [1:33.000] [Emilia- Romagna]. Ricerche Idrobiologiche nelle Valli di Comacchio. ll. Saggio cartografico della vegetazione delle Valli di Comacchio. *Ann. Univ. Ferrara* **1972**, *1*, 35–54.
55. Giaccone, G. Features and changes of the vegetation of the lagoons of the northern Adriatic Sea as a result of pollution. (Lineamenti della vegetazione lagunare dell'Alto Adriatico ed evoluzione in conseguenza dell'inquinamento). *Boll. Mus. Civico Storia Nat. Venezia* **1974**, *26*, 87–98.
56. Facco, S.; Degobbis, D.; Sfriso, A.; Orio, A.A. Space and Time Variability of Nutrients in the Venice Lagoon. In *Estuarine Variability*; Wolfe, D.A., Ed.; Academic Press, Inc.: New York, NY, USA, 1996; pp. 307–318.
57. Pavoni, B.; Marcomini, A.; Sfriso, A.; Donazzolo, R.; Orio, A.A. Changes in an Estuarine Ecosystem. The Lagoon of Venice as a Case Study. In *The Science of Global Change*; Dunnette, D.A., O'Brien, R.J., Eds.; American Chemical Society: Washington, DC, USA, 1992; pp. 287–305.
58. Sfriso, A.; Marcomini, A. Gross primary production and nutrient behaviours in shallow lagoon waters. *Bioresour. Technol.* **1994**, *47*, 59–66. [CrossRef]
59. Sfriso, A.; Buosi, A.; Tomio, Y.; Juhmani, A.-S.; Facca, C.; Wolf, M.; Sfriso, A.A.; Franzoi, P.; Scapin, L.; Bonometto, A.; et al. Environmental restoration by aquatic angiosperm trans-plants in transitional water systems: The Venice Lagoon as a case study. *Sci. Total Environ.* **2021**, *795*, 148859. [CrossRef]
60. Sørensen, T.H.; Vølund, G.; Armah, A.K.; Christiansen, C.; Jensen, L.B.; Pedersen, S.T. Temporal and spatial variations in concentrations of sediment nutrients and carbon in the Keta Lagoon, Ghana. *West Afr. J. Appl. Ecol.* **2003**, *4*, 91–105.
61. Lopez, P.; Lluch, H.; Vidal, M.; Morguí, S.A. Adsorption of phosphorus on sediments of the Balearic islands (Spain) related to their composition. *Estuar. Coast. Shelf Sci.* **1996**, *42*, 185–196. [CrossRef]
62. Pedersen, O.B.; Christiansen, C.; Laursen, M.B. Wind induced longterm increase and shortterm fluctuations of shallow water suspended material and nutrient concentration, Ringkøbing fiord, Denmark. *Ophelia* **1995**, *41*, 273–287. [CrossRef]
63. de la Lanza-Espino, G.; Flores-Verdugo, F.J.; Hernandez-Pulido, S.; Penié-Rodríguez, I. Concentration of nutrients and C:N:P ratios in surface sediments of a tropical coastal lagoon complex affected by agricultural runoff. *Universidad y Ciencia Trópico Húmedo* **2011**, *27*, 145–155.
64. Gomez, E.; Millet, B.; Picot, B. Accumulation des sels nutritifs dans un sediment lagunaire et environnement hydrody-namique. *Oceanol. Acta* **1998**, *21*, 805–817. [CrossRef]
65. Zayas, R.G.-D.; Yera, A.B.; Artiles, M.M.; González, J.A.L.; Sandoval, F.S.C.; Merino-Ibarra, M. Trace metals in sediments of seven coastal lagoons of the Sabana-Camagüey Archipelago, Cuba. *Soil Sediment Contam. Int. J.* **2021**, *30*, 331–349. [CrossRef]