

Benthic nutrient cycling at the sediment-water interface in a lagoon fish farming system (northern Adriatic Sea, Italy)

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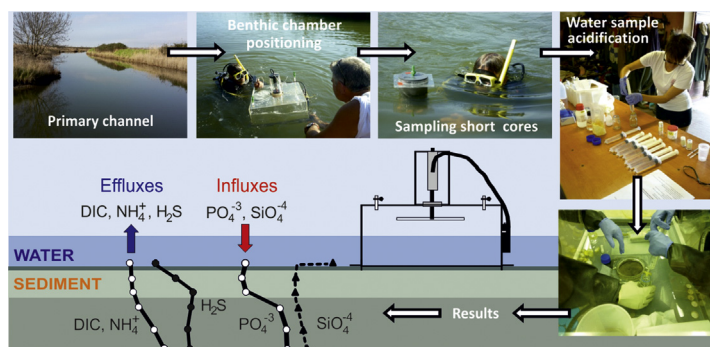
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HIGHLIGHTS

- The trophic status of a fish farm was investigated in a lagoon environment.
- Metabolism and nutrient fluxes were seasonally studied on site with a benthic chamber.
- Environmental conditions can be extreme with persistent hypoxic-anoxic events.
- Toxic organic forms of chemicals may be transferred into the aquatic food chain.
- Nutrients remineralisation needs to be mitigated by better hydrodynamism.

GRAPHICAL ABSTRACT



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ABSTRACT

Metabolism and carbon, oxygen, and nutrient fluxes (DIC, DOC, DO₂, NO₂⁻, NO₃⁻, NH₄⁺, PO₄³⁻ and SiO₄⁴⁻) were studied during three surveys at two sites (VN1 and VN3) located at a fish farm at the Marano and Grado Lagoon (northern Adriatic Sea), using an *in situ* benthic chamber. Field experiments were conducted in July and October 2015 and March 2016 at a depth of approximately 2 m along the main channels of the fish farm. Water samples were collected by a scuba diver every 2 h in order to investigate daily fluxes of solutes across the sediment-water interface (SWI). Regarding the solid phase, C_{org}/N_{tot} and C_{org}/P_{org} molar ratios suggested an autochthonous marine origin of the organic matter and a minor preservation of P in the sediments, respectively; high values of sulphur (S_{tot}) were also encountered (0.8–2%). The conditions at VN3 were mostly anoxic with high NH₄⁺ levels (30–1027 μM) and the absence of NO₃⁻. Substantial daily patterns of all solutes occurred especially in autumn and winter. On the contrary, fluxes at VN1 were less pronounced. Usually, inverse correlations appeared between dissolved O₂ and DIC trends, but in our system this was observed only at VN3 in autumn and accomplished by a parallel increase in NH₄⁺, PO₄³⁻ and SiO₄⁴⁻ during intense nutrient regeneration. These results are significantly different than those reported for open lagoon environments, where nutrient regeneration at the SWI and in surface sediments is the primary source of nutrients available for assimilation processes, especially during the warmer period of the year when the natural nutrient input by fresh water inflows is limited. Due to the importance of

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1. Introduction

Coastal lagoons are recognised as transitional environments among marine, freshwater and terrestrial ecosystems. Due to their shallowness and because sunlight reaches the bottom, intense benthic primary production and respiration occur, thus enhancing the accumulation/recycling of both organic carbon and nutrients (Nowicki and Nixon, 1985; McGlathery et al., 2001; Cloern, 2001). Here, particle material deposited in sediment is actively decomposed and the transformation products (e.g., nutrients and DOC) are released in the upper water column (Grenz et al., 2010). A portion of these products becomes available for bacterial and phytoplankton production that ultimately may sink to the bottom sediments, once again fuelling the benthic communities (Soetaert et al., 1996). One of the main aspects of these processes is represented by the increase in aerobic microbial activity, which determines a decrease in oxygen levels and hypoxic/anoxic conditions in sediments, except at the sediment-water interface (SWI) or around the infaunal burrows (De Vittor et al., 2012). Regarding nutrients, nitrogen (N_2), nitrite (NO_2^-), and ammonium (NH_4^+) are released in waters during the denitrification process (Kemp et al., 1997), whereas phosphorus in its dissolved form (PO_4^{3-}) increases after the reduction of insoluble $FePO_4$ into more soluble $Fe_3(PO_4)_2$ (Ogrinc and Faganeli, 2006; Belias et al., 2007). The supply of nutrients in coastal waters is often a consequence of human activities such as agriculture, urbanisation and industrialisation and, over the last 30 years, aquaculture (Roselli et al., 2009). In the case of aquaculture, an excess of food provided to the fish held in cages, together with the pellets and metabolic products, frequently form a “nepheloid” sediment layer, which covers large surfaces of the bottom sediments causing hypoxic and/or anoxic conditions (Belias et al., 2003, 2007). Effects on benthic communities and alterations in concentration gradients between the water column and surface sediments induce changes in the oxygen and nutrient fluxes at the sediment-water interface (SWI), which can also influence the rates of nitrate reduction processes within the sediment (Dunn et al., 2013 and references therein). An increase in the natural concentrations of nutrients (DIN and phosphate) and changes in their seasonal patterns (Šestanović et al., 2016), can, in the most extreme cases, cause eutrophication phenomena. Enhanced nutrient supplies promote an immediate increase in the abundance of both autotrophic and heterotrophic microbial groups and chlorophyll *a*, often associated with negative consequences for benthic bacteria and benthic fauna (Šestanović et al., 2016 and references therein).

In the lagoons of the northern Adriatic, aquaculture practices, especially fish farming, have taken place since the 19th century. This change in the lagoon usage has been achieved through several man-made embankments which heavily alter the original morphology and hydrodynamics, thus influencing the turnover of organic matter and nutrients (D'Aiotti et al., 2007). There are two main types of fish farming: extensive and intensive. Extensive farming uses only the trophic resources available in the environment. Intensive farming involves farm workers feeding the fish in order to have a higher yield in a shorter time period. This latter method, however, has a greater impact upon the environment.

Val Noghera, one of the most important fish farms, was characterised by D'Aiotti et al. (2007) in a one-year monitoring study. The results drew attention to high NH_4^+ levels in the water column, which is toxic to fish. There is, however, still a lack of knowledge regarding nutrient cycling through the SWI as well as the general trophic status in a closed lagoon ecosystem modified for aquaculture purposes such as a fish farm. For these reasons, the aim of this work was to study the benthic biogeochemical cycling of nutrients (NO_2^- , NO_3^- ,

NH_4^+ , PO_4^{3-} , SiO_4^{4-}), inorganic and organic carbon (DIC and DOC), dissolved oxygen (O_2) and hydrogen sulphide (H_2S) at the SWI, estimating benthic and diffusive fluxes at two different sites using an *in situ* deployed light benthic chamber (Fig. 1). This approach has been widely employed in the Gulf of Trieste (Bertuzzi et al., 1996, 1997; Covelli et al., 1999), Venice Lagoon (Sfriso et al., 1992; Sfriso et al., 1995; Sfriso and Marcomini, 1997, 1999), Po delta lagoons (Barbanti et al., 1992a, 1992b; Viel et al., 1991), and Grado and Marano Lagoon (De Vittor et al., 2012).

The final objectives were to identify possible critical factors affecting the management of the fish farm and to suggest a series of best available practices to improve upon the ecological and chemical status of this aquatic environment.

2. Materials and methods

2.1. Study area and sampling strategy

The Marano and Grado Lagoon (northern Adriatic Sea, Italy) is located between the Tagliamento and Isonzo River deltas and it extends for approximately 32 km reaching a width of up to 5 km ($A = 160 \text{ km}^2$). Freshwater inputs are very scarce and mostly limited to the western sector (Marano lagoon). The estimated overall amount of average freshwater discharge is approximately $70\text{--}84 \text{ m}^3 \text{ s}^{-1}$ and is mostly from the Stella River (Sladonja et al., 2011). In addition, thirty drainage pumps, mainly located along the coastal plain, contribute to water discharge from irrigation canals.

The Marano and Grado Lagoon is one of the best conserved wetlands in the entire Mediterranean area. This system is classified as a coastal microtidal lagoon of large dimensions (Italian Decree n. 131/08) and has been protected by the Ramsar Convention since 1971. Following the implementation of the Habitats Directive (92/43/EC), it was also designated as a Site of Community Importance (SCI - IT3320037) (Acquavita et al., 2015). The lagoon and the neighbouring mainland host socio-economic activities (e.g., industrial sites, commercial harbours, marinas, fishing, fish and clam farming, and tourism), which pose environmental concerns in terms of priority pollutants (Ramieri et al., 2011).

The western sector of the lagoon (Marano) is polluted by nitrates (NO_3^-) from intensive agricultural and other anthropogenic activities. This sector was designated as a NO_3^- vulnerable zone (NVZ), where an action plan to address the reduction of NO_3^- leaching was initiated (Saccon et al., 2013). Recently, a 1-year cycle of physical and chemical measurements (nutrients, chlorophyll *a*, dissolved oxygen, temperature and salinity) was conducted in the whole lagoon area with the aim of assessing its trophic state (Acquavita et al., 2015). The authors have asserted that the considerable spatial and temporal variability of nutrients occur mainly in the form of nitrogen (N) carried inland through river discharges into the Marano basin. These inputs of nutrients were compensated by the water exchange with the adjacent open sea, which exerted a dynamic dilution effect and induced low water residence time thus limiting nutrient enrichment and accumulation for long periods of time. The molar Redfield ratio (DIN/SRP) (Redfield et al., 1963) was always higher than the optimum value of 16 (in some cases up to 2000), thus suggesting that the system is phosphorus (P) limited, as confirmed by low chlorophyll *a* content, rare algal blooms and good water oxygenation. Trophic state indices and threshold values were applied. A broad range of classes was found (from oligotrophic to hypertrophic), thus suggesting that over simplification of this complex ecosystem should be avoided.

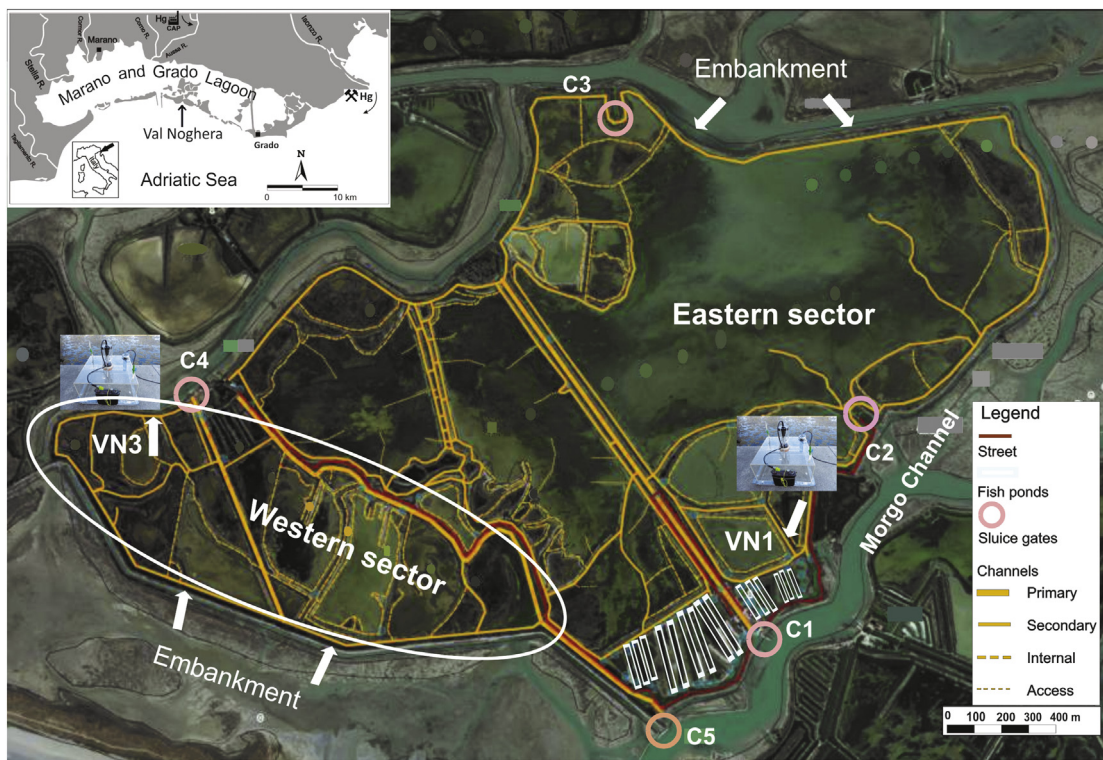


Fig. 1. The study area: the Val Noghera fish farm. The investigated sites (VN1 and VN3) in two primary channels and the sluice gates are reported.

Regarding the primary production in the Marano and Grado Lagoon, Blasutto et al. (2005) suggested that it depends upon the benthic microalgal community due to the inexhaustible nutrient supply from the sediment porewater (Granéli and Sundbäk, 1985 and references therein). The highest production rates were found in the more “marine” Grado Lagoon, where the low salinity fluctuation rather than freshwater inputs favoured the establishment of a more stable and less stressed microphytobenthic community, recently determined as being mainly composed of diatoms (Bacillariophyceae), dominantly benthic (82%), with a few indeterminate flagellates (Blasutto et al., 2005).

The Val Noghera fish farm totals 2.7 km² in size and is located in the central sector of the lagoon, where the construction of embankments has allowed for the isolation of part of the lagoon from the surrounding environment (Fig. 1). Fresh groundwaters at temperatures up to 33 °C flow from several artesian wells into the fish farm in order to reduce the salinity in summer and to mitigate the very cold surface water temperature in winter.

Taking into consideration the structure of the fish farm, two main sectors coexist which differ significantly from one another (Fig. 1). The western sector ($A = 0.6 \text{ km}^2$) was cut off from the surrounding lagoon environment at the end of the 19th century. Here, fish farming makes use of extensive practices and water circulation is limited and accomplished by a scarce exchange with the external lagoon through two of the five sluice gates (C4 and C5, Fig. 1). The eastern sector of the fish farm was created in the 1960s. The water exchange and circulation are assured by the periodic opening of two sluice gates: gate C1 is manually opened in flood tide conditions to let the waters flow in, whereas the waters automatically flow out through sluice gate C2 during ebb tide. Gate C1 is located near the fish ponds (Fig. 1). Here, feeding activities take place until the fish, gilthead seabream (*Sparus aurata*) and seabass (*Dicentrarchus labrax*), reach adequate commercial size (in one or two years).

Based on these differences, two experimental sites were selected in order to evaluate benthic nutrient cycling at the SWI, the first in the eastern sector (VN1) and the second in the western sector (VN3).

Preliminary monitoring was carried out at each site (VN1 and VN3) by employing a multiparameter probe (SMATCH) in order to assess the long-term variability of the main environmental parameters. The multiparameter probe was located at VN1 (45°42'36.78"N 13°18'29.83"E) from September to October 2014 (03/09/14 to 07/10/14), and at VN3 (45°42'49.80"N 13°17'15.27"E) from October to November 2014 (06/10–13/11). The probe was placed at a depth of about 20–30 cm from the bottom to continuously measure (every 30 min) temperature, pH, Eh, conductivity, and dissolved oxygen in depth (see Section 3.1).

2.2. Sampling

A transparent *in situ* benthic chamber was successfully used in previous studies conducted in the Gulf of Trieste (Bertuzzi et al., 1997; Covelli et al., 1999) and in the Marano and Grado Lagoon (Covelli et al., 2008; De Vittor et al., 2012), to assess nutrient cycling at the SWI. A detailed description of the apparatus is reported in Covelli et al. (2008). In the present study three experiments were performed: July 2015, October/November 2015, and February/March 2016, corresponding to summer, autumn, and winter seasonal conditions, respectively.

The benthic chamber was put into place by a scuba diver and water samples were collected using polypropylene syringes through a flexible polyethylene tube at approximately 2-h time intervals (from $T_0 = 0$ to $T_f = 8 \text{ h}$), filtered through 0.45 μm pore size Millipore Millex HA membrane filters. Water samples were frozen to determine nutrient and DOC concentrations; while HgCl_2 (100 μL in 40 mL sample) and Zn acetate (100 μL in 40 mL sample) were added to determine DIC and H_2S , respectively, in the water samples before storing them at 4 °C. At the same time, the main chemical and physical parameters of water (pH, redox potential, dissolved oxygen, temperature, and conductivity) were recorded using a multiparameter probe (Crison PH 25) inserted therein.

Concurrently with the benthic chamber experiments, two short sediment cores were collected in order to characterise the sediment, extract pore waters and subsequently, to calculate diffusive fluxes at the SWI.

2.3. Analyses of solid phase

Sediment cores were extruded and sectioned into five slices (0–1, 1–2, 2–3.5, 3.5–5 and 5–7 cm) in a N₂-filled chamber to preserve the original redox conditions. Supernatant water had also been collected previously before sectioning. Porewaters were obtained by centrifugation at *in situ* temperature (3400 rpm; *t* = 30 min), filtered through membrane filters (0.45 mm pore size, Millipore Millex HA), and stored at 4 °C for several days until subsequent analyses following a specific protocol. In parallel, solid-phase samples were divided into subsamples for grain-size analyses, and carbon, nitrogen, phosphorus, and sulphur determinations.

For grain-size analysis, a subsample (15–20 g) of fresh sediment was treated with H₂O₂ (10%) for a minimum of 24 h to eliminate most of the organic matter. Subsequently, the sediment was wet sieved through a 2 mm sieve to remove coarse shell fragments. The resulting <2 mm fraction was analysed using a laser granulometer (Malvern Mastersizer, 2000).

Carbon, nitrogen, phosphorus, and sulphur were determined using freeze-dried (Scanvac, CoolSafe 55-4) samples, ground with a mortar and pestle and sieved through a 420 µm screen to be homogenised.

Total carbon (C_{tot}) and total nitrogen (N_{tot}) were determined using a Costech ECS 4010 Elemental Combustion System at a combustion temperature of 1020 °C, whereas organic carbon (C_{org}) was determined at 920 °C (Hedges and Stern, 1984), prior to progressive acidification with 0.1–1.0 M HCl, using the same instrument. Acetanilide was used as a standard compound for calibration. Analyses of total sulphur (S_{tot}) were performed using a CHNS elemental MICRO CUBE analyser (Elementar Analysensysteme GmbH, Hanau, Germany) at a combustion temperature of 1020 °C. The detection limit for C_{org} and C_{tot} was 0.1% and the precision for S_{tot} was 3%.

Total phosphorus (P_{tot}) was extracted from samples ignited at 550 °C for 2 h, and subsequently treated with 1 M HCl for 16 h under continuous agitation. The organic fraction (P_{org}) was found by calculating the difference in P content of 1 M HCl extracts before and after ignition of samples as reported in Aspila et al. (1976). The analysis of the extracts was conducted using standard methods for PO₄³⁻ as reported in the dissolved phase section.

Biopolymeric carbon (BPC, as a sum of carbohydrate (CHO), protein (PRT), and lipid (LIP) carbon) was determined according to the method used by De Vittor et al. (2016 and references therein).

2.4. Analyses of dissolved phase

Nutrient analyses, including nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺), phosphate (PO₄³⁻) and silicate (SiO₄⁴⁻), were performed using a segmented flow autoanalyser (Bran + Luebbe Quattro) following the methods reported in Grasshoff et al. (1999) and modified for the specific instrument. The detection limits calculated were 0.02 µM for NH₄⁺, NO₂⁻, NO₃⁻, and 0.01 µM for PO₄³⁻. Certified standards (Inorganic Ventures Standard Solutions and MOOS-2, NRC) were used to ensure the accuracy of the procedures. In addition, the laboratory performance was periodically checked through proficiency testing (PT) exercises organised by the European network of PT providers (QUASIMEME programmers AQ1 and AQ2).

H₂S was determined spectrophotometrically, after trapping with Zn acetate, as reported in Grasshoff et al. (1999). The reproducibility of the method was 5%.

Dissolved inorganic (DIC) and organic (DOC) carbon were determined using the Shimadzu TOC V-CSH analyser as reported in De Vittor et al. (2016). For DIC, samples were injected into the instrument port and directly acidified with phosphoric acid (25%). For DOC analysis, water samples were first acidified (automatically into an instrument syringe, 2% - 6 M HCl) and after CO₂ elimination, the concentration was determined using a high temperature catalytic method (Sugimura and

Suzuki, 1988). Analyses showed a variation coefficient < 2%. The reproducibility of the method was between 1.5 and 3%.

2.5. Diffusive and benthic flux calculations

Diffusive fluxes (F) represent an instantaneous measure of the flux of solutes diffusing from sediment porewaters to the overlying water column (supernatant water) along a concentration gradient. Positive values are indicative of an efflux, whereas negative values represent influxes or scavenging from the water column to the sediment particles. The calculation in this work follows Fick's first law and the details reported in De Vittor et al. (2012). Benthic fluxes, obtained via benthic chamber sampling, were calculated as reported in De Vittor et al. (2016).

3. Results and discussion

3.1. Monitoring campaigns of the water column before core sampling and benthic chamber experiments

Generally, the physical and chemical parameters of the water are strongly influenced by atmospheric events; temperature, wind intensity and rainfall patterns (data from OSMER ARPA FVG, www.osmer.fvg.it) were therefore recorded during water monitoring using a multiparameter probe (see Section 2.1. Study area and sampling strategy).

Some substantial differences were found between the two sites investigated (Figs. S1 and S2).

Station VN1 demonstrated daily fluctuations of dissolved oxygen content (O₂) with the minimum observed in the morning and increasing trends related to water temperature. This behaviour is likely due to the photosynthetic processes of microphytobenthos, as shown by significant peaks in the supersaturation of the water (Fig. S1). Moderate hypoxia conditions (O₂ approximately 2–5 mg L⁻¹) were recorded when air temperature decreased a maximum of 4 °C, wind speed increased and the inflow of waters stopped once the sluice gates were closed. Salinity changes were also lower than those observed in the open lagoon system.

At VN3, anoxic events persisting for four days were recorded using a multiparameter probe (Fig. S2), whereas in response to an increase in wind intensity, oxygen increased and the water cooled. When the temperature increased (up to 17 °C), the anoxic episodes towards the end of the recorded period occurred. Salinity was less variable than at VN1 and showed marine characteristics (up to 32 units PSU).

Overall, comparing the two sites, VN3 appears to be the more critical of the two due to the persistent anoxic conditions and the scarce water exchange that certainly affect this environment.

3.2. Occurrence of total, organic and biopolymeric carbon, nitrogen, phosphorus and sulphur in the sediments

According to the Shepard (1954) textural classification, VN1 and VN3 showed a predominance of silt (about 70%) and sand (10–15%). No clear pattern was observed moving downcore, however sand contents were significantly higher at VN3 (*p* < 0.01).

C_{tot}, C_{org} and N_{tot} contents were similar with depth and no differences were found year round at VN1, whereas at VN3 significant variations were shown for C_{org} and N_{tot}, especially in summer (from 3.99 to 1.55% and from 0.51 to 0.18%, respectively) moving downcore (Table 1) and in winter, when the highest values were found (3.42–4.38%) (Petranich et al., 2018). Also the N_{tot} displayed the highest values at VN3 in winter (0.40–0.55%), even if a decreasing trend was detected at both sites, ranging between 0.14 and 0.31% at VN1 and between 0.18 and 0.55% at VN3. Goñi et al. (2003) established that a C_{org}/N_{tot} molar ratio > 14 is typical of organic matter (OM) of a terrestrial origin depleted in nitrogen-containing biochemicals and enriched in carbon (i.e. lignin and cellulose), whereas a ratio < 10 can be associated with marine-derived OM (i.e. phytoplankton and

Table 1Redox potential, total and organic carbon and phosphorous, total nitrogen and sulphur and $C_{\text{org}}/N_{\text{tot}}$ and $C_{\text{org}}/P_{\text{tot}}$ molar ratio in the sediments of the two investigated sites.

Site	Season	Level (cm)	Eh (mV)	C_{tot} (%)	C_{org} (%)	N_{tot} (%)	$C_{\text{org}}/N_{\text{tot}}$	P_{tot} (%)	P_{org} (%)	$C_{\text{org}}/P_{\text{org}}$	S_{tot} (%)
VN1	Summer	0–1	–417	6.16	2.09	0.25	9.75	0.034	0.017	321	0.93
		1–2	–424	5.87	2.07	0.23	10.5	0.040	0.021	252	1.10
		2–3.5	–427	5.65	1.85	0.21	10.5	0.037	0.017	278	1.05
		3.5–5	–436	5.68	2.34	0.30	9.10	0.043	0.024	256	1.08
		5–7	–439	5.59	2.57	0.31	9.83	0.028	0.012	556	0.97
	Autumn	0–1	87	6.01	1.98	0.21	11.0	0.031	0.017	301	0.82
		1–2	–35	5.86	2.11	0.22	11.4	0.036	0.022	251	1.17
		2–3.5	–360	5.91	2.02	0.20	11.8	0.039	0.024	213	1.74
		3.5–5	–370	6.14	1.73	0.16	12.6	0.030	0.017	260	1.04
		5–7	–438	6.58	1.55	0.14	12.9	0.028	0.015	262	1.03
	Winter	0–1	–259	5.74	2.73	0.25	12.7	0.036	0.024	299	1.03
		1–2	–428	5.44	2.57	0.30	10.0	0.039	0.027	250	1.25
		2–3.5	–448	5.43	2.61	0.29	10.7	0.044	0.031	218	1.26
		3.5–5	–434	5.52	2.46	0.27	10.8	0.042	0.029	219	1.27
		5–7	–435	5.44	2.58	0.29	10.5	0.042	0.029	226	1.02
VN3	Summer	0–1	–401	7.42	3.99	0.51	9.22	0.054	0.035	291	1.49
		1–2	–387	6.66	2.08	0.39	6.30	0.044	0.027	198	1.50
		2–3.5	–367	6.00	1.85	0.25	8.79	0.036	0.021	229	1.53
		3.5–5	–372	5.83	1.95	0.19	11.9	0.032	0.017	288	1.55
		5–7	–383	5.77	3.14	0.18	20.4	0.032	0.017	480	1.53
	Autumn	0–1	–398	6.11	2.95	0.33	10.6	0.039	0.026	299	1.89
		1–2	–401	6.01	2.90	0.30	11.3	0.039	0.026	292	1.99
		2–3.5	–402	5.83	2.66	0.29	10.9	0.037	0.025	279	1.19
		3.5–5	–403	5.51	2.43	0.25	11.6	0.039	0.027	236	1.88
		5–7	–405	5.56	2.40	0.24	11.9	0.035	0.023	265	1.92
	Winter	0–1	–419	7.27	4.31	0.55	9.13	0.053	0.040	276	1.39
		1–2	–422	6.77	3.42	0.46	8.77	0.051	0.039	229	1.46
		2–3.5	–425	6.62	3.60	0.42	10.0	0.047	0.034	271	1.64
		3.5–5	–426	6.71	4.38	0.50	10.2	0.047	0.037	309	1.71
		5–7	–425	6.02	3.44	0.40	10.2	0.044	0.033	266	1.79

bacterioplankton), characterised by a higher nitrogen content (Ogrinc et al., 2003). In this work, the ratio was highest in autumn (mean 11.9 ± 0.79) and variable with depth at VN1. Similar results were found at VN3, with the exception of summer ($C_{\text{org}}/N_{\text{tot}} = 20.4$, 5–7 cm level) where faster nitrogen degradation may have occurred, thus suggesting that the OM is mainly of autochthonous marine origin as already observed in other abandoned fish farms (Covelli et al., 2008). The concentrations are notably higher than those reported for the open lagoon likely due to the significant input of OM related to aquaculture activities and remineralisation of labile organic detritus (De Vittor et al., 2012 and references therein). Generally, P_{tot} and P_{org} decreased with depth at both sites in all seasons with the highest values found in winter, up to 0.044% and 0.031% at VN1 and up to 0.053% and 0.040% at VN3, respectively. The average $C_{\text{org}}/P_{\text{org}}$ molar ratios, which showed irregular trends moving downcore, varied between 213 and 556 at VN1 and between 198 and 480 at VN3 (Table 1). The ratios were twice that of those found by De Vittor et al. (2012) in the Marano Lagoon (175–251), thus suggesting a minor preservation of P in sediments from this fish farm, which appeared depleted in P relative to the living marine organic matter, but lower than those of the Grado Lagoon ($C_{\text{org}}/P_{\text{org}}$ maximum value, 973).

Regarding the S_{tot} content, high values (0.8–2%) were found compared to those of the Grado Lagoon (Covelli et al., 2008) (0.19 and 0.69%). As previously stated, these elevated S_{tot} contents may originate from the reduction and degradation processes of the OM, which form several low molecular weight S compounds (Cutter and Krahforst, 1988) that accumulate at the SWI.

The sediment concentrations of biochemical compounds, $\text{CHO}_{\text{H}_2\text{O}}$ and CHO_{EDTA} , PRT, LIP, and BPC (as a sum of the carbon of the four components) along the sediment depth differ significantly among seasons at both stations ($\text{CHO}_{\text{H}_2\text{O}}$: $p < 0.01$; CHO_{EDTA} : $p < 0.01$; PRT: $p < 0.01$; LIP: $p < 0.005$; BPC: $p < 0.005$) (Fig. S3). On average, surface sediments (0–1 cm) at station VN3 were characterised by a 1.5–2.7 fold higher concentration of all components than at station VN1 with the exception of CHO_{EDTA} , while similar values characterised the deeper layers. This could be related to the scarce water exchange which favours the accumulation of OM, mainly due to the settlement of organic rich fine

sediments (Cividanes et al., 2002) and to the extremely anoxic conditions at VN3 which cause a higher density of decaying infaunal organisms providing additional easily degradable “fresh” OM to microbes (Riedel et al., 2014). As a consequence of the anoxic mineralisation (Koron et al., 2015), porewater NH_4^+ and PO_4^{3-} levels were also higher in the surface sediments at this station (Fig. 3). Even if the relative percentage composition differs slightly among seasons and along the sediment depth, the BPC was dominated by PRT at both stations ($67.7 \pm 10.7\%$ and $67.4 \pm 9.3\%$, at VN1 and VN3, respectively) followed by LIP ($15.4 \pm 6.7\%$ and $21.1 \pm 6.7\%$) and CHO_{EDTA} ($13.2 \pm 3.3\%$ and $7.8 \pm 4.2\%$). $\text{CHO}_{\text{H}_2\text{O}}$ contributed to the total BPC only for $3.6 \pm 1.8\%$ and $3.8 \pm 1.2\%$ at VN1 and VN3, respectively.

At VN1, PRT ranged from 2771 to 10,798 $\mu\text{g C g}^{-1}$ showing an increasing gradient with depth in the first 5 cm, LIP ranged from 623 to 1925 $\mu\text{g C g}^{-1}$ displaying irregular vertical profiles as well as CHO_{EDTA} , which varied between 745 and 2015 $\mu\text{g C g}^{-1}$. $\text{CHO}_{\text{H}_2\text{O}}$ profiles were quite uniform except for the maximum found at 1–2 cm in autumn (183–554 $\mu\text{g C g}^{-1}$).

At VN3, PRT ranged from 1901 to 11,474 $\mu\text{g C g}^{-1}$ (the maximum was reached at the surface during summer), LIP varied between 440 and 4237 $\mu\text{g C g}^{-1}$ displaying a decreasing gradient with depth, CHO_{EDTA} decreased with depth only in autumn while showing highly variable vertical profiles during the other seasons with a concentration range of 212–1355 $\mu\text{g C g}^{-1}$. $\text{CHO}_{\text{H}_2\text{O}}$ concentrations (range 113–658 $\mu\text{g C g}^{-1}$) decreased with depth in autumn and summer, while a slight increase was found in winter at level 2–3.5 cm.

The dominance of proteins in the BPC pool has been reported in the northern Adriatic Sea (Danovaro et al., 2000; Dell'Anno et al., 2003; Cibic et al., 2012) as well as for other coastal sediments (for a review, see Pusceddu et al., 2009) and is considered a specific feature of eutrophic environments (Danovaro et al., 2000). Since proteins are more readily utilised by bacteria than carbohydrates, a high PRT/CHO ratio suggests the presence of OM recently generated and vice versa (Danovaro et al., 1993). PRT/CHO ratios are significantly high at surface sediments (0–2 cm) at VN3 indicating the presence of a high amount of living OM or newly-produced detritus probably due to the low hydrodynamism.

BPC vertical profiles reflected patterns observed for protein concentrations. The BPC represented, on average, the $46 \pm 14\%$ of C_{org} at station VN1 and its contribution to C_{org} generally increased with depth up to layer 3.5–5 cm.

The biopolymeric fraction at station VN3 constituted on average $33 \pm 15\%$ of the total C_{org} , showing significantly high variability in contribution both along the sediment depth and among the seasons. Increasing accumulation of BPC in marine sediments, even in highly productive systems such as estuaries, ponds, and fish farm sediments, is associated with low algal carbon contributions to BPC. This suggests that in eutrophic sediments characterised by high BPC concentrations and benthic algal biomass, algal carbon is progressively diluted in a complex and heterogeneous organic matrix (Pusceddu et al., 2009).

3.3. Dissolved inorganic and organic carbon, hydrogen sulphide and nutrients in porewaters

Porewater DIC concentrations were comparable, from 2.65 to 13.6 mM at VN1 and from 3.36 to 13.7 mM at VN3, and generally

showed an increase with depth at both sites more evident during winter (Fig. 2). Since DIC represents the ultimate product of C_{org} oxidation (Alperin et al., 1999), its increase may be mostly attributed to processes associated with the decomposition of OM (Lojen et al., 2004) that occurs within the sediment column. This behaviour was previously reported in both marine (De Vittor et al., 2016) and lagoon (Covelli et al., 2008; De Vittor et al., 2012) areas. Moreover, the carbonate system in waters (seawater, porewaters from marine sediments) is controlled by pH, alkalinity and salinity. If two of the four measurable parameters, such as pH, alkalinity, total CO_2 (DIC) and partial pressure of CO_2 (PCO_2) are known, the marine carbonate system can be characterised (Millero, 2005). Since the pH in porewaters of surface sediments from the Gulf of Trieste is nearly constant (7.7–8.0), the system appears to be well buffered by carbonate minerals. The contribution of carbonate dissolution to DIC benthic fluxes increases in summer, when the oxidation of sulphides forms strong sulphuric acid and may contribute to $\frac{1}{4}$ of DIC (Ogrinc et al., 2003). Hence, the DIC variation in the surface of the northern Adriatic sediments can largely be attributed to processes associated with the decomposition of OM.

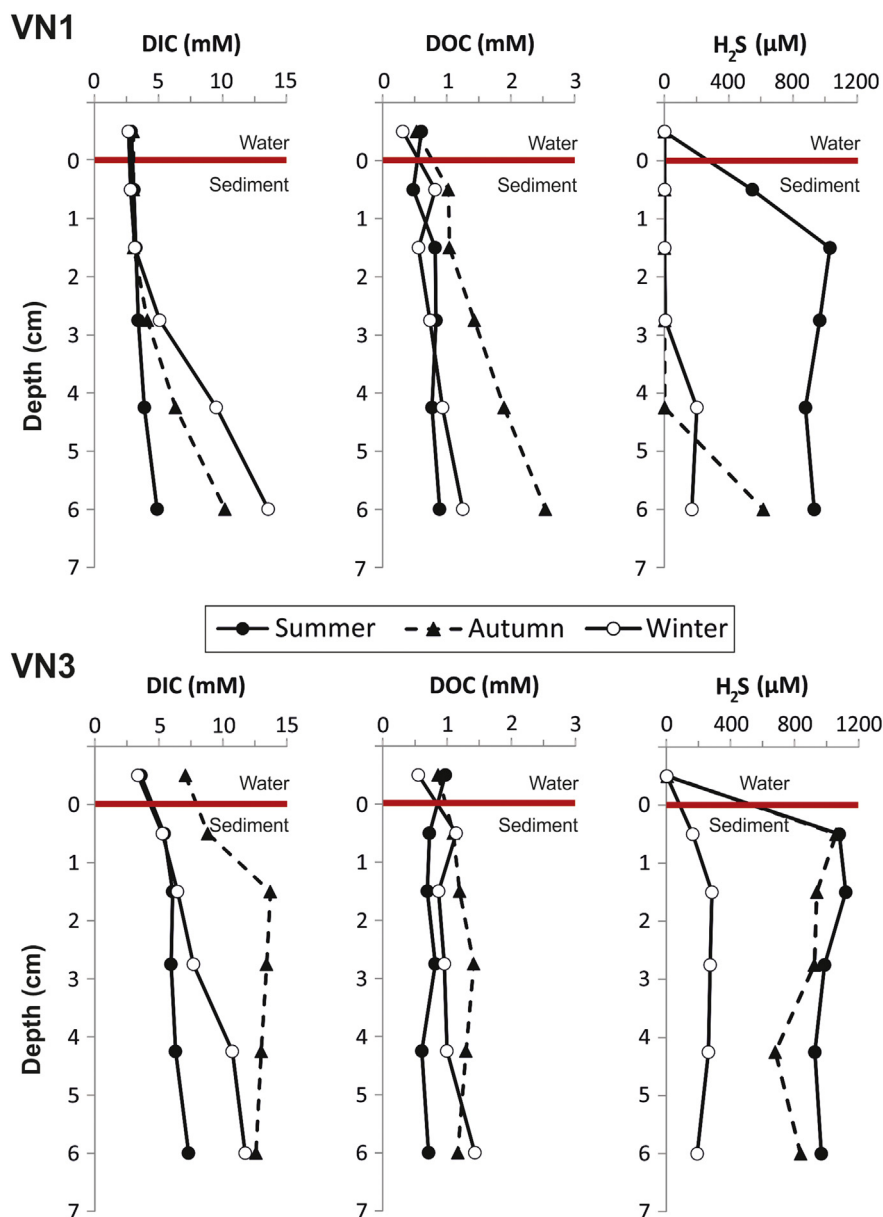


Fig. 2. Seasonal vertical profile in the sediment porewaters of DIC, DOC and H_2S at sites VN1 and VN3.

DOC profiles were almost constant with depth with the exception of site VN1 in autumn (2.54 mM at 5–7 cm). These results indicate that DOC is prevalently in macromolecular (humic) form, thus exhibiting a subsequent low mobility from the solid phase (Burdige et al., 1992). Moreover, the absence of an irregular trend suggests that the intensity of biological mixing is lower than that previously found at other lagoon sites (Covelli et al., 2008; De Vittor et al., 2012).

Hydrogen sulphide also showed a marked increase from supernatant to 1–2 cm level, more evident in summer, then slightly decreased with depth at both sites. Site VN3 was characterised by significantly ($p < 0.01$) higher values (up to 1120 μM , 1–2 cm) than VN1. Covelli et al. (2011) also observed a constantly increasing trend in sediment porewaters of the Grado Lagoon, where H_2S showed concentrations much lower and in a narrow range (1.5–15 μM), than those of this work (0.03–1120 μM). The highest concentrations found in the upper sediment levels could be explained by the degradation and mineralisation of OM, mostly by sulphate reducing bacteria which typically occur when the redox potential falls to approximately -200 mV (Wildish et al., 1999). In this study, the Eh exceeds -400 mV already in the first levels to remain constant with depth. According to these processes, similar trends between H_2S and DIC were observed, with significant correlations in VN1 porewaters in autumn ($r = 0.917$, $p < 0.05$) and in winter ($r = 0.917$, $p < 0.05$). The H_2S decreasing trends with depth and NO_2^- , NO_3^- and DOC throughout the core were observed and can be attributed to benthic bioturbation and to the very quick reactions of reactive iron with sulphide, leading to FeS precipitation

(Middelburg and Levin, 2009), reducing the sulphide diffusion from the deepest anoxic sediment levels (De Vittor et al., 2016).

Dissolved nutrients showed similar trends at both sites (Fig. 3). Taking into consideration the dissolved inorganic nitrogen (DIN), NH_4^+ represented the predominant form ranging from 60.1 and 97.6% at VN1 and from 84.7 to 97.7% at VN3 (up to 1259 and 1075 μM , respectively), due to the reduced sediment conditions and increased moving downcore more markedly in summer and winter at VN3. Nitrite was negligible, thus the oxidised forms are depicted as their sum ($\text{NO}_2^- + \text{NO}_3^-$). A steep positive gradient was found from the supernatant water to the first level (0–1 cm) analysed, whereas moving downcore the concentrations remained constant probably due to the equilibrium between the early diagenesis of OM and nitrification processes enhanced by infaunal bioturbation activity (De Vittor et al., 2012). Ammonium profiles paralleled those for the DIC, also showing a direct correlation in the winter season ($r = 1.000$, $p < 0.001$) due to active OM degradation (Ogrinc and Faganeli, 2006), as evidenced by Eh values found in the deepest levels (Table 1) and by the H_2S vertical profiles. The N pool, however, was notably higher than that reported for other lagoon areas (De Vittor et al., 2012).

Phosphates showed a net increase downcore at both sites as observed for NH_4^+ (Fig. 3). The two chemical species were strongly correlated both at VN1 and VN3 during all seasons. The PO_4^{3-} concentrations were always higher than those observed at the Artalina fish farm (2.6–20 μM), the Grado (average 4.25 μM) and Marano (average 20.7 μM) Lagoon. The ratio $\text{NH}_4^+/\text{PO}_4^{3-}$ can provide information about the processes of

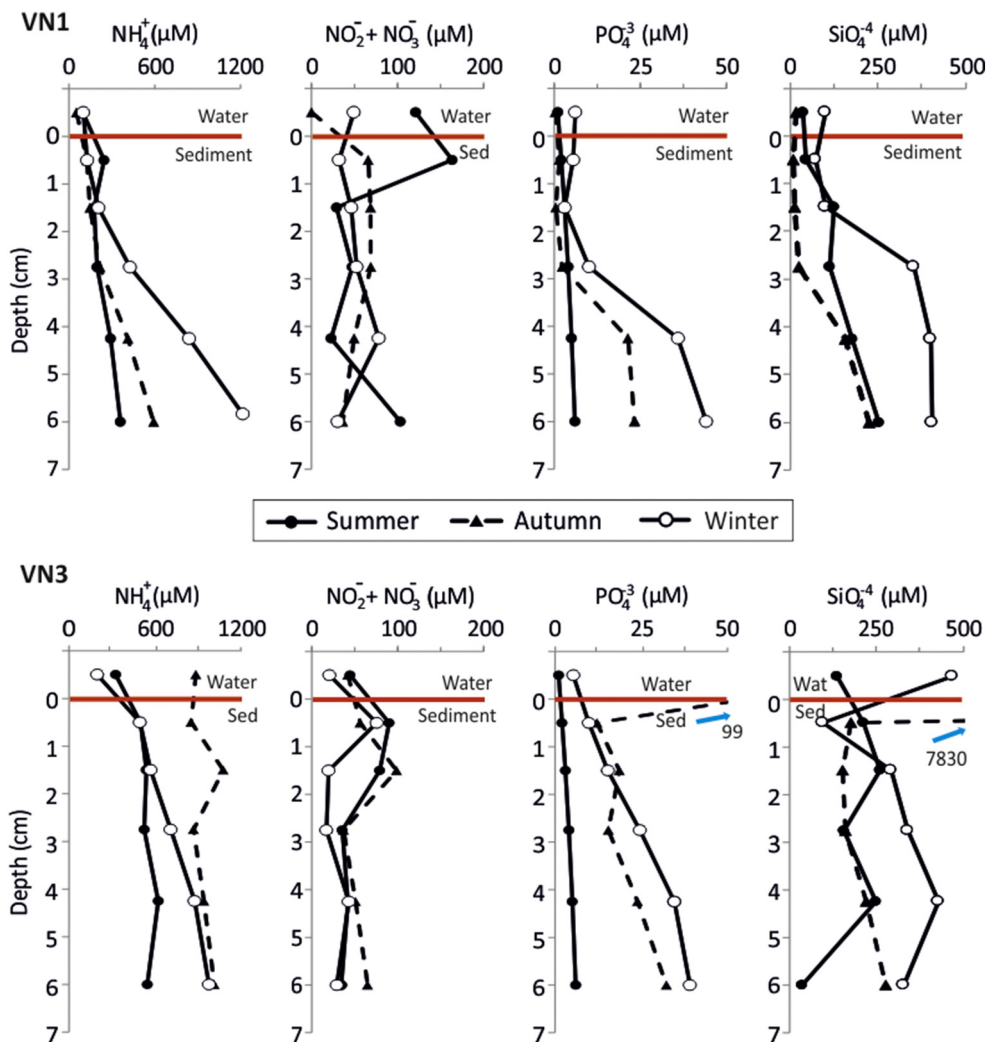


Fig. 3. Seasonal vertical profile in the sediment porewaters of NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} and SiO_4^{4-} at sites VN1 and VN3.

release/uptake of the latter from/in the solid phase (Anschutz et al., 2007; De Vittor et al., 2016). The ratio varied from 16.6 to 352 at VN1 and from 8.9 to 70 at VN3. This suggests that the mineralisation of OM alone cannot explain the profiles and that in the surface sediments reactions involving P removal, such as adsorption on Fe-oxides (De Vittor et al., 2012), precipitation as authigenic P mineral, and biological uptake within the sedimentary column occurred (Belias et al., 2007). The decrease in the ratio with depth confirmed the release of PO_4^{3-} from reduced Fe-oxides and the anaerobic mineralisation of organic P (Sundby et al., 1992).

Similarly, SiO_4^{4-} concentrations also increased with depth at both sites, showing values higher than those found in the Marano Lagoon (<500 μM , in De Vittor et al., 2012), and other coastal systems (Belias et al., 2007; De Vittor et al., 2012, 2016). This could originate from the dissolution of biogenic Si of the protective coating of diatom siliceous structures accumulated in the sediment over time (Zhang et al., 2013). The dissolution of biogenic silica is a simple physicochemical process strictly dependent on temperature, pressure, pH and specific surface area of the solid silica source (e.g. diatom frustules). In particular, dissolution rate increases nearly two orders of magnitude with rising temperature and pressure, which usually occur in the deepest sediment levels (Canfield et al., 2005). The low SiO_4^{4-} concentrations observed at the SWI are likely due to the assimilation of silica, previously remineralised and accumulated in the porewaters, by microphytobenthos (Welker et al., 2002). As observed for PO_4^{3-} and NH_4^+ , similar trends were depicted between SiO_4^{4-} and PO_4^{3-} and between SiO_4^{4-} and NH_4^+ , also showing significant direct correlations in autumn at site VN1 ($r = 0.917$ $p < 0.01$ and $r = 1.000$, $p < 0.001$, respectively).

3.4. Diffusive fluxes at the sediment-water interface

Diffusive fluxes are reported in Table 2. Positive values indicate net effluxes, whereas the negative values are representative of net influxes. Generally, a net efflux involved most of the solutes, which was more marked at VN3 especially in summer and winter periods (as seen in bold type in Table 2).

DIC and DOC generally showed effluxes, with the exception of summer at both sites for DOC (-0.15 and -0.30 $\text{mmol m}^{-2} \text{d}^{-1}$ at VN1 and VN3, respectively). This suggests that DOC was utilised as fast as it was produced (De Vittor et al., 2012, 2016). The effluxes of NH_4^+ were up to four times higher than the NO_3^- effluxes. As reported by Berner (1980), the increase in microbial reactions is capable of enhancing the molecular diffusion rate. In our study, the reduction of NO_3^- to NH_4^+ could be the result of both denitrification processes and dissimilatory NO_3^- reduction that releases NH_4^+ in sediment porewaters, which quickly diffuses along a concentration gradient towards the upper water column (Lerat et al., 1990).

PO_4^{3-} and SiO_4^{4-} also showed the highest effluxes in summer at both sites. Anoxic conditions, attested to by the H_2S effluxes (Middelburg and Levin, 2009), are the main cause of the biomass degradation by anaerobic bacteria, which releases water soluble forms of N and P and eventually some Si. Phosphate effluxes were very low (0.003 – 0.024 $\text{mmol m}^{-2} \text{d}^{-1}$) similar to that reported by De Vittor et al. (2012), and an influx occurred at VN3 (-0.23 $\text{mmol m}^{-2} \text{d}^{-1}$) in autumn. SiO_4^{4-} influxes were found in

autumn and winter probably in relation to Si uptake by benthic microalgae. It could be hypothesised that Si, originating from the dissolution of protective coatings of diatom siliceous structures accumulated in sediment and dissolved in porewaters, is moved along the concentration gradient accumulating in the supernatant water (Belias et al., 2007). McManus et al. (1995) suggested that the dominant process controlling porewater silicate could be the solubility of the bulk biogenic silica, the solubility of the most soluble biogenic silica fraction, or surface silica reactions involving aluminium (Li and Schoonmaker, 2003).

3.5. Benthic chamber experiments

It is noteworthy that the first sampling took place outside the chamber possibly near the SWI. Conversely, the other samples were collected inside the chamber at approximately 15 cm from the SWI. This step was necessary in order to avoid possible interference due to the re-suspension of sediments, which could occur immediately after the positioning of the chamber by the scuba divers.

The dissolved oxygen variability showed different seasonal patterns at VN1 (Fig. 4) as already observed at another fish farm (Covelli et al., 2008). During summer, a constant increase from 61.6 to 102 μM (1.97 – 3.27 mg L^{-1}) was observed, likely due to the daily photosynthetic activity. Conversely, the winter and autumn results were characterised by a decrease, thus suggesting that the microbial respiration prevails over the dissolved O_2 production by photosynthesis (De Vittor et al., 2012). Despite the low dissolved O_2 , it was possible to identify a net decrease from 103 to 3.44 μM (3.3 – 0.11 mg L^{-1}) at VN3 only in winter. Regarding H_2S , seasonal variations were found at both sites, whereas the highest levels were measured at VN3 (up to 215 μM). At VN1, clear opposite trends were observed with respect to dissolved O_2 , especially in winter ($r = -0.333$), although correlations were not statistically significant ($p > 0.05$) considering each season. On the contrary, due to the dissolved O_2 depletion in the benthic chamber, the relationship at VN3 was less evident.

Similar and constant trends of DIC were found at both sites (2.23 – 2.51 and 2.43 – 4.29 mM at VN1 and VN3 respectively) in all seasons, excluding only the autumn campaign at VN3, where a marked increase (from 2.84 to 10.2 mM) was observed. An inverse trend between diurnal O_2 and DIC variations was commonly found (Covelli et al., 2008; De Vittor et al., 2012, 2016), due to the coupling between photosynthetic and respiration processes. Here, a decoupling between DIC and dissolved O_2 at both sites was observed likely due to habitat-dependent factors such as the non-photosynthetic incorporation of CO_2 , chemosynthetic removal of dissolved O_2 (Johnson et al., 1981), and carbonate precipitation (Cermelj et al., 2001). DOC patterns demonstrated marked differences seasonally at both sites with concentrations up to one order of magnitude lower than DIC. Similar DIC/DOC patterns were observed only at VN3 (autumn), but no significant correlation was found (Fig. 4). This behaviour could be justified by the anaerobic decomposition of OM at the SWI, which causes the release of DIC to the water column and DOC after degradation of its macromolecular (i.e. humic acid) components (Burdige et al., 1992; Alperin et al., 1999). No correlation was found either for DOC or dissolved O_2 , as previously reported for the Marano and Grado Lagoon (Covelli et al., 2008; De

Table 2
Diffusive fluxes at sites VN1 and VN3.

Site	Season	mmol $\text{m}^{-2} \text{d}^{-1}$								
		DIC	DOC	NH_4^+	NO_2^-	NO_3^-	$\text{NO}_2^- + \text{NO}_3^-$	PO_4^{3-}	SiO_4^{4-}	H_2S
VN1	Summer	1.12	-0.15	1.35	0.019	0.36	0.38	0.024	0.07	28.56
	Autumn	0.10	0.53	0.61	0.011	0.52	0.52	0.003	-0.07	0.011
	Winter	0.83	0.54	0.22	-0.003	-0.14	-0.14	-0.002	-0.17	-0.001
VN3	Summer	10.22	-0.30	1.62	0.003	0.42	0.42	0.024	0.57	55.513
	Autumn	8.84	0.26	-0.28	0.016	0.10	0.12	-0.229	-53.60	49.629
	Winter	11.37	0.75	2.96	0.000	0.53	0.53	0.014	-3.05	1.141

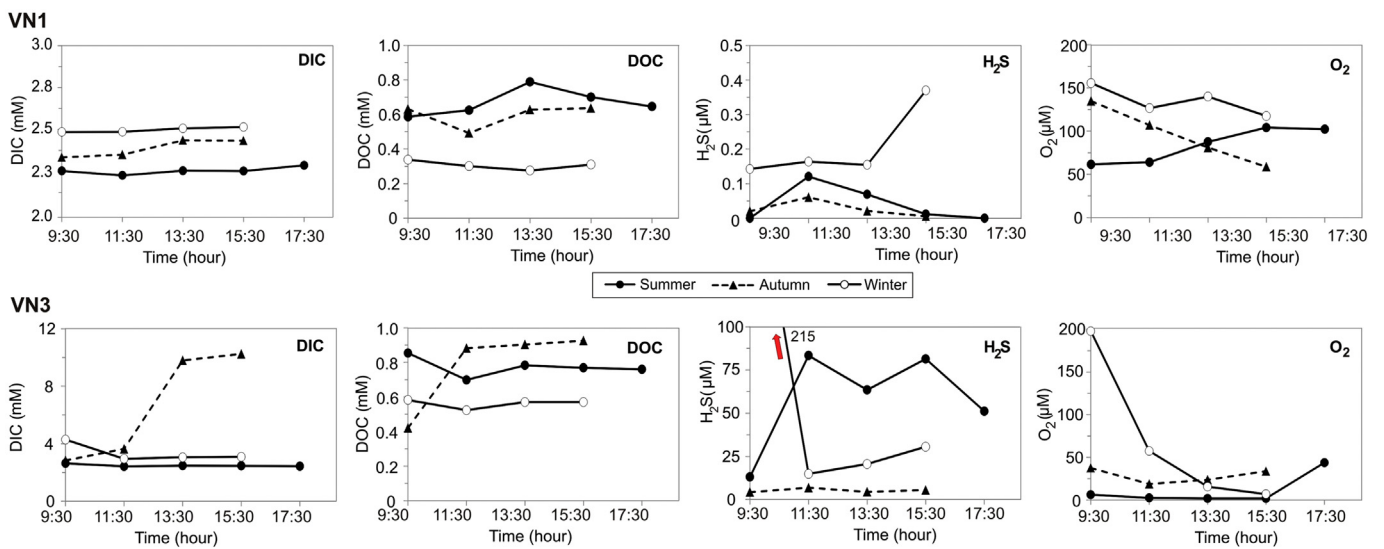


Fig. 4. Daily variations of DIC and DOC in mM, H₂S and dissolved O₂ in μM in the benthic chamber at sites VN1 and VN3 in different seasons. Note that DIC and H₂S concentrations are reported using different scales between the two sites.

Vittor et al., 2012). This is typical of the lagoon environments where the simultaneous presence of different biological processes occasionally occurs. The increase in primary production does not directly lead to net accumulation of DOC, which might instead be due to other biological activities. For instance, DOC might originate from organic substance aerobic degradation and from the benthic release of the dissolved organic matter (DOM) or by extracellular photosynthetates (Ogawa et al., 2003).

Taking nutrients into consideration, it should be noted that at VN3, which was characterised by extremely anoxic conditions, a high level of NH₄⁺ was found and that this exceeded the first measurement taken inside the chamber (Fig. 5). Both NO₂⁻ and NO₃⁻ represented the minor fraction of the DIN pool. However, at VN1 where less extreme redox conditions occurred, NO₃⁻ accounted for about 42% of the pool and NO₂⁻ contents were almost negligible. For this reason, these oxidised forms have been considered together as a sum in the graphic in Fig. 5. During summer, these forms were undetectable, whereas

they reached the highest levels at VN3 (98 μM) in autumn. It is noteworthy that despite the NO₃⁻ seasonal variations (<10–98 μM), NO₂⁻ was never completely consumed. This most likely indicates the coexistence of two processes: (1) the complete consumption of NO₃⁻ could be due to autotrophic uptake during diurnal incubations and, (2) the presence of NO₂⁻ is the result of denitrification processes by NO₃⁻ reducing bacteria, which is the preferred bacterial metabolic pathway for energy production favoured by decreasing O₂ levels (Belias et al., 2007). Ammonium represented almost the total of the DIN pool (96–99.9%) at both sites in summer, showing high percentages in other seasons as well (54–99%), mostly at site VN3 (91–99%). Excluding the first steep decrease, all forms of N showed poor variability over time, excluding the autumn sampling at VN3 inside the chamber. The variations of NH₄⁺ inside the chamber show a slight increase, and NO₂⁻ + NO₃⁻ an opposite trend, which could be associated with denitrification processes. However, faster oxidation during sampling operations in the field could justify the increase in NO₂⁻ + NO₃⁻ levels at VN3 in autumn,

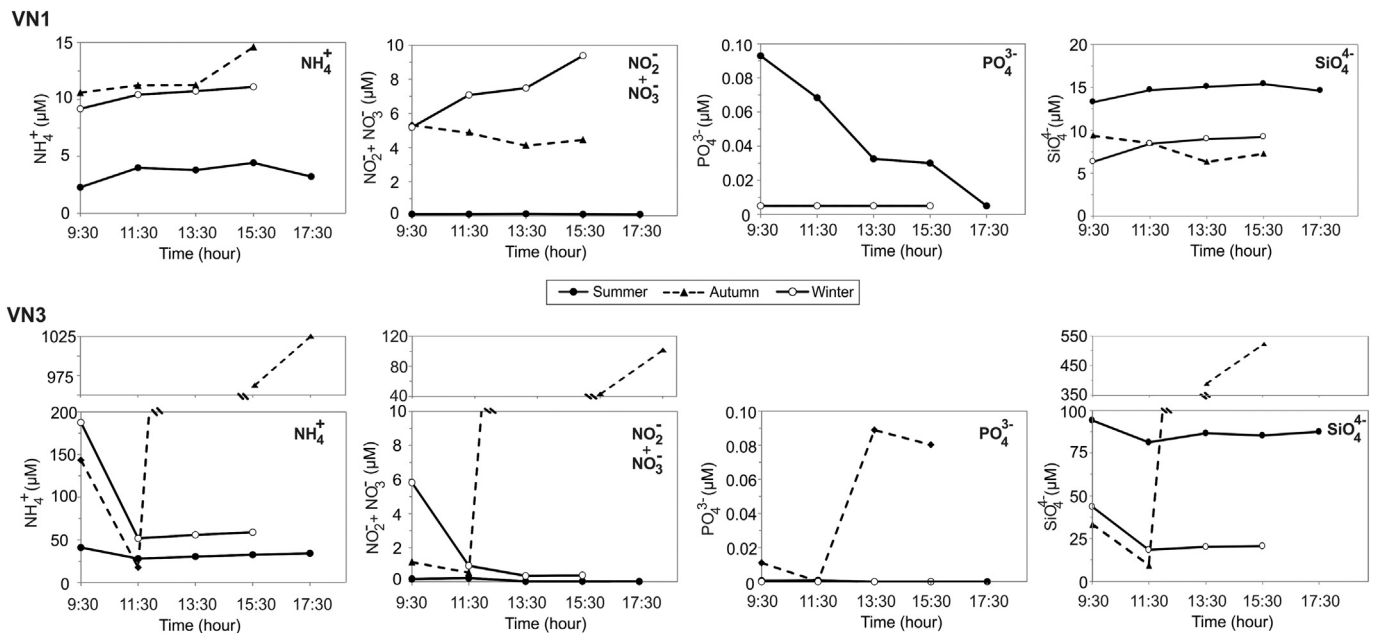


Fig. 5. Daily variations of NO₂⁻, NO₃⁻, NH₄⁺, PO₄³⁻ and SiO₄⁴⁻ in the benthic chamber at sites VN1 and VN3 in different seasons.

where NH_4^+ values could even be underestimated. When trends moved in the same direction, a simultaneous influence of denitrification (sediment)/nitrification (oxygenated water) processes and algal uptake can be hypothesised (De Vittor et al., 2016). In addition, several biogeochemical processes including the uptake by phytoplankton and benthic microalgae, excretion by zooplankton and bacterial remineralisation, which play an important role in nitrogen cycling, can also occur (Roselli et al., 2009). Similar trends among these N forms are described in De Vittor et al. (2012).

Generally, phosphate levels found in this study were very low and varying in a narrow range ($< \text{lod}$ – $0.20 \mu\text{M}$), with the exception of the autumn period at VN3 and the summer period at VN1, where increasing (from 0.04 to $22.2 \mu\text{M}$) and decreasing (from $0.09 \mu\text{M}$ to $< \text{lod}$) trends were observed respectively. These results are comparable to those previously obtained by Covelli et al. (2008) and De Vittor et al. (2012) in the Grado Lagoon (from $< \text{lod}$ to $0.49 \mu\text{M}$). These exceptions are likely due to different dissolved O_2 trends observed at each site. In fact, the increase of dissolved O_2 at VN1 likely caused the oxidation of Fe (II) to Fe (III) with the subsequent formation of insoluble FePO_4 and adsorption or coagulation to precipitating into colloidal iron hydroxides $[\text{Fe}(\text{OH})_x]$ (Scoullou et al., 1987). On the contrary, at VN3 where anoxia increased, the opposite reaction (Fe (III) to Fe (II) reduction) caused the release of PO_4^{3-} into the overlying water (Scoullou et al., 1987; Waldebeck et al., 1988).

The $\text{DIN}/\text{PO}_4^{3-}$ ratio was always higher than the proposed Redfield ratio (16:1) (Redfield et al., 1963), varying from 25 to 251, at VN1 and from 45 to 432, at VN3. These values suggest that P is the limiting nutrient for microalgal production for the majority of the year. A similar situation was also found by Bertuzzi et al. (1997) in the sediments of the Gulf of Trieste and by Sundback et al. (2000) in microtidal shallow-water sediments. Ogrinc and Faganeli (2006) support that high $\text{DIN}/\text{PO}_4^{3-}$ ratios could also be attributed to PO_4^{3-} precipitation as phosphate minerals, e.g. apatite.

Silicate values were 80 times higher at VN3 (9.61 – $517 \mu\text{M}$) than VN1 (6.26 – $15.4 \mu\text{M}$). As already stated, anoxic conditions accelerate the dissolution of biogenic Si from diatom siliceous structures accumulated in the sediment (Belias et al., 2007). At both sites, SiO_4^{4-} trends were comparable with those of $\text{NO}_2^- + \text{NO}_3^-$ and NH_4^+ in all seasons, showing a marked increase at VN3 in autumn similar to PO_4^{3-} . Only during the autumn campaigns a significant correlation between SiO_4^{4-} and NH_4^+ was found at VN3 ($r = 1.000$, $p < 0.05$) and between SiO_4^{4-} and $\text{NO}_2^- + \text{NO}_3^-$ at both sites ($r = 1.000$, $p < 0.01$ and $r = 1$, $p < 0.05$, at VN1 and VN3, respectively), thus suggesting that benthic diatoms preferentially assimilate NH_4^+ rather than NO_3^- . On the other hand, the fact that NH_4^+ trends follow that of $\text{NO}_2^- + \text{NO}_3^-$ in some cases (even if not significantly correlated, $p > 0.05$) suggests that nutrient fluxes are also controlled by external factors such as the bioirrigation rate (Berelson et al., 2013).

3.6. Benthic fluxes at the sediment-water interface

Fluxes calculated from chamber experiments as daily total fluxes (Rasheed et al., 2006) differed substantially from diffusive fluxes (Table 3), resulting in three orders of magnitude higher. The fluxes of dissolved O_2 , DIC and DOC were found to be close to positive (i.e., directed to the water column), with the exception of dissolved O_2 in autumn ($-26 \text{ mmol m}^{-2} \text{ d}^{-1}$) and in winter ($-5 \text{ mmol m}^{-2} \text{ d}^{-1}$) at VN1, and in winter at VN3 ($-15 \text{ mmol m}^{-2} \text{ d}^{-1}$). The highest O_2 fluxes were found at both sites in summer whereas the highest for DIC and DOC in autumn, excluding DOC at VN3 which showed a maximum value in summer ($33 \text{ mmol m}^{-2} \text{ d}^{-1}$). DIC and DOC fluxes were found to be positive in summer, most likely because respiration and photosynthesis processes were in balance and DOC product was most likely not in the labile form. On the other hand, in autumn the O_2 influxes corresponded to high DIC and DOC effluxes at both sites, which could be due to respiration processes and phytoplankton and benthic

Table 3
In situ benthic fluxes at sites VN1 and VN3.

Benthic fluxes					
Site	Parameters		Photoperiod		
			Summer	Autumn	Winter
VN1	O_2	$\text{mmol m}^{-2} \text{ d}^{-1}$	20	-26	-5
	DIC	$\text{mmol m}^{-2} \text{ d}^{-2}$	31	45	16
	DOC	$\text{mmol m}^{-2} \text{ d}^{-2}$	11	79	5
	H_2S	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-63	-30	117
	N-NH_4^+	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-400	1840	390
	N-NO_2^-	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-9	-66	8
	N-NO_3^-	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	0	-153	1300
	$\text{N-(NO}_2^- + \text{NO}_3^-)$	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-9	-219	1310
	P-PO_4^{3-}	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-33	0	0
	Si-SiO_4^{4-}	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-61	-1050	709
VN3	O_2	$\text{mmol m}^{-2} \text{ d}^{-1}$	11	4	-15
	DIC	$\text{mmol m}^{-2} \text{ d}^{-2}$	8	3450	81
	DOC	$\text{mmol m}^{-2} \text{ d}^{-2}$	33	23	28
	H_2S	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-17,070	-713	9260
	N-NH_4^+	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	3250	528,320	4190
	N-NO_2^-	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-104	2080	78
	N-NO_3^-	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	0	50,830	-404
	$\text{N-(NO}_2^- + \text{NO}_3^-)$	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-104	52,920	-327
	P-PO_4^{3-}	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	-104	10,480	0
	Si-SiO_4^{4-}	$\mu\text{mol m}^{-2} \text{ d}^{-2}$	4990	407,540	1900

microalgae metabolism, as well as the plasmolysis of algae that can cause DOC production (Naudin et al., 2001; Vignudelli et al., 2004), as found by De Vittor et al. (2012).

H_2S fluxes were found to be negative in summer and autumn and positive in winter at both sites with the maximum values at VN3. Fluxes of H_2S and dissolved O_2 clearly showed an opposite behaviour, as water depleted in O_2 is accompanied by an increase in H_2S , even if the two parameters were not significantly correlated ($p > 0.05$), probably due to the onset of the hypoxic/anoxic conditions that stimulate the reduction processes at the SWI.

Nitrite fluxes were negligible whereas nitrate fluxes were quite variable at both sites in all seasons, with the highest fluxes obtained in autumn at VN3 (2082 and $50,834 \mu\text{mol m}^{-2} \text{ d}^{-1}$, respectively), which also demonstrated the highest NH_4^+ efflux ($528,317 \mu\text{mol m}^{-2} \text{ d}^{-1}$). This occurs when denitrification and remineralisation processes dominate over nitrification, although NO_2^- and NO_3^- did not show a negative flux in this case. The NH_4^+ effluxes were observed at both sites in all campaigns, indicating the degradation of sedimentary organic N (Belias et al., 2007; De Vittor et al., 2012). An influx was obtained only in summer at VN1 ($-400 \mu\text{mol m}^{-2} \text{ d}^{-1}$), which could be due to a high O_2 efflux oxidising NH_4^+ (nitrification). PO_4^{3-} influxes were observed at both sites during the summer, while a high efflux was calculated ($10,480 \mu\text{mol m}^{-2} \text{ d}^{-1}$) at VN3 in autumn. Under oxic conditions, PO_4^{3-} is bound to sediments in Fe-Mn-phosphate complexes, as occurred in summer, which are rapidly desorbed under anoxic conditions. The release during periods of good oxygenation, as shown by dissolved O_2 efflux at VN3 in autumn, is the result of fast and short periods of high respiration and subsequent nutrient regeneration, since high NO_2^- and NO_3^- effluxes were observed. The PO_4^{3-} flux variations are also linked to organic P degradation, as observed in the sediments from the Gulf of Trieste (Ogrinc and Faganeli, 2006), to authigenic formation of P minerals and to P utilisation by phytoplankton, bacteria and benthic microalgae, since P is recognised as a limiting nutrient in the northern Adriatic Sea (Degobbis et al., 2005). Phosphate release, the regeneration of which from sediments is a slow process (Liu et al., 2004) and the exchanges of which are largely controlled by the oxygen status of the sediment (Rizzo, 1990), was observed only at VN3, likely due to the degradation of sedimentary organic P rather than at VN1. The SiO_4^{4-} benthic fluxes were governed by microbial and chemical dissolution of opal (Canfield et al., 2005), dependent on redox conditions, assimilation by benthic diatoms and flocculation and coprecipitation of silicon polymers and clay minerals with Fe (III)

(Belias et al., 2007). The highest SiO_4^{4-} effluxes were measured at site VN3 in autumn ($265,786 \mu\text{mol m}^{-2} \text{d}^{-1}$), while at VN1, an efflux was observed only in winter ($462 \mu\text{mol m}^{-2} \text{d}^{-1}$). The release SiO_4^{4-} from the sediment is likely associated to dissolution processes of biogenic Si, as already observed with the high diffusive fluxes. Conversely, the in-fluxes at VN1 could be due to the benthic diatom silicate uptake.

3.7. Recommendations on management of the fish farm in the lagoon environment

Persistent anoxic events ($\text{O}_2 < 1 \text{ mg L}^{-1}$), which are not mitigated by rainfall and wind, and the high temperature occurring during summer with the formation of algal blooms can create critical conditions not only for the benthic community, but also for the entire aquatic food chain. In addition, the high occurrence of dissolved NH_4^+ concentration, which is a toxic species, should not be underestimated. The main recommendation that arises from this study is that the accumulation of nutrients in the fish farm and the biogeochemical processes involved in their remineralisation should be mitigated by better hydrodynamism in order to improve the quality status of this aquatic system. Possible solutions could be simple adjustments such as mechanical aeration systems inside the channels and the fish ponds coupled with the construction of new sluice gates to increase water renewal. This could help increase the oxygenation of the water column thus reducing the hypoxic-anoxic events along with the negative effects on the biogeochemical cycles of nutrients in the fish farm. A parallel study conducted on mercury cycling (Petranich et al., 2018) in the same fish farm demonstrated that bottom sediments, especially in anoxic conditions, are a significant source of methylmercury, the most toxic organic form, into the water column where it eventually accumulates and may be bioavailable to be transferred into the aquatic food chain. Enhancing water dynamics could also mitigate those conditions which are more suitable for mercury methylation and bioaccumulation.

4. Conclusions

The long-term *in situ* monitoring of the water column showed that the western sector of the fish farm is subject to oxygen depletion at the SWI due to the scarce water exchange with the open lagoon and the limited vertical mixing of the water column. Rainfall and strong winds are presently the only natural factors which can help in improving the general quality status of the aquatic environment. The importance of processes associated with the decomposition of OM may be inferred from the distribution of nutrients in porewaters. The extremely high levels of H_2S (up to $1250 \mu\text{M}$) and NH_4^+ (>95% of nitrogen species) are in agreement with the sediment reducing conditions. Benthic fluxes showed a strong remineralisation which produced high effluxes from the SWI for NH_4^+ ($528,317 \mu\text{mol m}^2 \text{d}^{-1}$), H_2S ($9257 \text{ mmol m}^2 \text{d}^{-1}$) and SiO_4^{4-} ($265,786 \mu\text{mol m}^2 \text{d}^{-1}$) especially where hydrodynamic conditions are critical.

In summary, the scarce water renewal and the enrichment of OM and nutrients may cause persistent eutrophication phenomena in the water column and an intense remineralisation at the sediment-water interface. The results of the field work in a lagoon fish farm clearly indicate that the magnitude and timing of these biogeochemical processes are significantly amplified in a confined lagoon environment. Possible mitigation procedures could and should be considered in this context for better management of the fish farm and to improve the ecological and chemical status of the environment.

Abbreviations

BPC	biopolymeric carbon
C_{org}	organic carbon
C_{tot}	total carbon
C-CHO	carbohydrate carbon

C-LIP	lipid carbon
C-PRT	protein carbon
DIC	dissolved inorganic carbon
DIN	dissolved inorganic nitrogen
DOC	dissolved organic carbon
H_2S	hydrogen sulphide
N_2	nitrogen
N_{tot}	total nitrogen
NH_4^+	ammonium
NO_2^-	nitrite
NO_3^-	nitrate
O_2	dissolved oxygen
OM	organic matter
P_{org}	organic phosphorous
P_{tot}	total phosphorous
PO_4^{3-}	orthophosphate
SRP	soluble reactive phosphorus
SiO_4^{4-}	orthosilicate
SWI	sediment-water interface
T	temperature

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Appendix A. Supplementary data

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