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Complex water column nutrient dynamics in the Gulf of Trieste; freshwater nutrient discharge Vs biologically mediated cycling of dissolved organic matter

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Chapter 1 Introduction

1.1. Anthropogenic influences on marine ecosystems

River dominated coastal ecosystems have received considerable attention in recent decades, often becoming the scenario of different eutrophication phenomena. Eutrophication of coastal ecosystems from nutrient over-enrichment is widespread (Nixon 1995) and inputs of anthropogenic nutrients into coastal seas have generally increased steadily (Moffat 1998) with the effects manifested in a myriad of direct and indirect responses (Cloern 2001). Coastal eutrophication is a major environmental threat worldwide (Wu 1999) and is arguably the biggest pollution problem facing estuaries globally (Howard et al. 2000). The frequency of eutrophic events such as noxious phytoplankton blooms and bottom water hypoxia has increased in many coastal areas, particularly in those influenced by riverine inflow and anthropogenic nutrient enrichment (Justic 1987). Besides the heavy effects on marine ecosystems, these events often represent a major cause of economic losses for coastal fisheries (Orel et al. 1986, 1993, Vitousek et al. 1997, Bricker et al. 1999) and tourism (Bricker et al. 1999, Fonda Umani et al. 2007). Eutrophication is most frequently described as enrichment of mineral nutrients (primarily nitrogen and phosphorus) to surface waters and as an increase in the rate of supply of organic carbon to an ecosystem (Nixon 1995). Within the EU, a common legislative approach defines eutrophication as the enrichment of water by nutrients, especially compounds of nitrogen and phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms and the quality of the water concerned (Urban Waste Water Treatment Directive, C.E.C. Council Directive 91/271/EEC. 1991).

The relative balance between supply and removal of nutrients determines which nutrient limits phytoplankton growth (Beman et al. 2005). To successfully mitigate eutrophication, one should be able to identify which nutrient(s) is/are responsible for enhanced primary production so that management actions can be focused on nutrients having the highest impact. An understanding of which nutrient(s) limit growth rates and biomass in the pelagic photic zone is essential, whether the perspective is from management of marine systems or from basic research in any of the disciplines of ocean biogeochemistry, pelagic food-webs, or the cell physiology of phytoplankton and bacterioplankton. Effective control of coastal marine eutrophication requires a variety of monitoring and both experimental and modelling research. Mesocosm studies offer an example of experimental model ecosystem approach to examine cause and effect relationships in marine systems. The basic idea with these approaches is to enclose the ecosystem under study. This normally requires a scaling down of the system and the inclusion of the relevant components in a much smaller space than that in which they normally occur in the wild. Thus, the problem lies in how to scale the miniature so that it can still function as a reasonable facsimile of the wild ecosystem (Wolff 2002). These small-scale studies are used to examine, for instance, nutrient limitation (Tamminen and Andersen 2007) and

community responses to nutrient enrichment (Olsen et al. 2006, Løvdal et al. 2008). Extrapolation of mesocosm studies into natural systems is not straightforward as the results of experiments can be affected by artificial boundaries (Sanford et al. 2001) and a lack or limited contact with sediment. Information on functioning of marine systems is also important for modeling purposes which can assist environmental managers in controlling eutrophication.

Ecological stoichiometry is a discipline that seeks to understand the balance of multiple chemical elements in ecological interactions. Redfield (1934) observed that marine phytoplankton contains a mol C:N:P ratio of 106:16:1 (50:7:1 by weight), since then, the use of elemental ratios has become widespread in marine and freshwater phytoplankton studies. A departure from this ratio has been assumed to imply nutrient deficiency. In such a case, there is not only sub-optimal growth of phytoplankton but also substandard food resources for primary consumers of phytoplankton. For diatoms that need silicate for their frustules, an optimal C:Si:N:P ratio of 106:15:16:1 has been suggested (Harrison et al. 1977). Nitrogen has been frequently inferred as the first limiting nutrient in open oceanic waters, while phosphorus has been inferred as the first limiting nutrient in many coastal zones, but co-limitation has also been reported. In spite of high anthropogenic loadings of nitrogen and phosphorus into coastal systems, phytoplankton may be nutrient limited due to an alteration in N:P, Si:P and Si:N ratios (Lopes et al. 2007 and references therein). Alterations in water N:P ratios may have significant impacts on aquatic communities beyond a simple reduction in phytoplankton productivity and biomass (standing stock), including shifts in species composition and possible selection for species adapted to growth in waters with reduced N:P ratios (Atkinson & Smith 1983). Intracellular toxin content in harmful algal bloom (HAB) species has been shown to increase when the cells grow under nitrogen and/or phosphorus unbalanced conditions in relation to their optimum (Flynn et al. 1994, Edvardsen & Paasche 1998, Johansson & Granéli 1999). Consequently, the knowledge of the spatial and temporal characteristics of dissolved nutrient concentrations and their ratios is a fundamental tool for the correct and sustainable management of critical areas such as regions of freshwater influence.

Phosphorus limitation of phytoplankton and/or bacterioplankton growth has been evidenced in several areas in the Mediterranean Sea (Krom et al. 1991, Thingstad and Rassoulzadegan 1995, Diaz et al. 2001, Sala et al. 2002, Zohary et al. 2005) and in the Adriatic (Degobbis 1990, Granéli et al. 1999, Marasović et al. 2005, Tedesco et al. 2007). In the Mediterranean basin there is a shortage of phosphorus because all the inputs to the system are significantly in excess of the Redfield N:P ratio of 16:1 (Krom et al. 2004), which is common for phytoplankton growth (Redfield et al. 1963). In the Adriatic, the excess of nitrogen over phosphorus is even stronger than in the rest of the Mediterranean (Chiaudani and Vighi 1982, Socal et al. 1999) due to the large imbalance delivered by the Po river (Lipizer et al. 1999, De Witt and Bendoricchio 2001). Therefore, on the basis of high N:P ratios in the seawater column and of bioassay studies (Chiaudani and Vighi 1982, Degobbis 1990, Granéli et al. 1999), phosphorus is regarded as the primary limiting nutrient in the Adriatic.

Contrary to the ultra-oligotrophic eastern Mediterranean, with its very low levels of primary productivity and very little organic matter production and accumulation (Krom et al. 2005), it has been suggested that fast regeneration processes of organic phosphorus in the Adriatic can contribute to the maintainment of phytoplankton growth thus explaining why very low concentrations of phosphate coupled with exceptional high chlorophyll *a* values can be found (Tedesco et al. 2007).
Phytoplankton abundance and distribution is largely dependent on nutrients and light availability but also on the stability of the water column. Coastal morphometry, i.e. such characteristics as mean depth, water surface area, volume, residence time and fetch, affects the flow of energy and nutrients through the coastal water ecosystem and thereby determines the sensitivity of a coastal water area to eutrophication (Wallin and Håkanson 1991).

1.2. Evaluating nutrient deficiency in marine waters by the determination of ectoenzyme activities

A possible indirect way of rapidly evaluating nutrient deficiency of the environment is by the determination of ectoenzyme activities, which can be synthesized by bacteria and by phytoplankton (Martinez and Azam 1993, Berges and Falkowski 1996, Stoecker and Gustafson 2003). Nutrient limitation may induce cells to synthesize ectoenzymes to enable the acquisition of the limiting nutrient (Hoppe 1983) and cells respond rapidly and directly to changes in nutrient and substrate availability by manipulating enzyme kinetics to best capitalise environmental conditions (Williams and Jochem 2006). Ectoenzyme activities may thus serve as a proxy for nutrient limitation, not by indicating the amount of the proper substrate present, but by pointing towards the physiological state of the cell or of the total microbial population. When phosphate concentration in the water drops below a critical threshold level, or when phytoplankton cell P quota decreases, the production of the alkaline phosphatase (APA) enzyme is induced in bacteria and phytoplankton, allowing the cells to utilize organically bound phosphorus (see review by Cembella et al. 1984). Alkaline phosphatase, the most active ectoenzymes in marine waters, hydrolyse a wide range of organic P compounds due to their low specificity for organic moiety compared to more specific phosphatases such as 5'-nucleotidases (Ammerman and Azam 1985), and has been used to indicate P deficiency in freshwater plankton communities (Chròst 1991, Brutemark et al. 2005) and in the marine environment as well (Thingstad et al. 1998, Cotner et al. 2000, Stihl and Sommer 2001, Vidal et al. 2003).
Amino peptidases (AMA) hydrolyze peptides and proteins, which comprise a major part (and probably the most utilizable fraction) of the marine organic N pool (Henrichs et al. 1984, Coffin 1989). Therefore, in order to bypass the use of biomass estimations, Sala et al. (2001) suggest the ratio between alkaline phosphatase and aminopeptidase activities (APA:AMA) as an indicator of N versus P limitation of the whole microbial community.
Several organism and processes may be considered as potential sources for the release of hydrolytic

enzymes dissolved in seawater. For example, cell lysis accompanied by grazing and virus infection on bacteria and plankton may release enzymes into seawater (Kerner et al. 1994, Mohapatra and Fukami 2004).

1.3. Problem & Strategy

The nutrient dynamics in the marine waters of the Gulf of Trieste are very complex and yet not completely understood. Like in the rest of the Mediterranean Sea, the production in the Gulf of Trieste is considered to be phosphorus-limited. This assumption is based mainly on very high inorganic N:P ratios but the important organic nutrient pool has not been considered. Further information is needed in order to understand the complex nutrient dynamics which depend on biologically mediated uptake/regeneration processes, physical forcing and freshwater nutrient input.
In order to evaluate of the importance of nutrient rich freshwater discharge into the Gulf of Trieste and to gain knowledge on the complex nutrient dynamics, following sampling strategy was decided:

Firstly; evaluation of temporal variation and spatial distribution of dissolved inorganic nutrients, dissolved organic nitrogen (DON) and phosphorus (DOP), particulate nitrogen (PN) and phosphorus (PP), Total Nitrogen (TN) and Phosphorus (TP), monitored on 12 sampling stations in the Gulf.

Secondly; to study the temporal evolution of inorganic nutrients and TN and TP content in the Timavo River, the second most important river discharging to the Gulf.

Thirdly; investigation on different time-scales of the dynamics of eco-enzymatic alkaline phosphatase (APA) and amino peptidase activities (AMA) and organic/inorganic nutrients at a coastal station (C1), in order to answer the question: Can the eco-enzymatic activities, monitored on different time-scales, add important new information on these dynamics, and how important are these activities to the system compared to nutrient rich freshwater discharge?

Chapter 2. Spatial distribution and temporal variation of nutrients.

2.1. Introduction

Like in the rest of the Mediterranean Sea, the primary production in the Gulf of Trieste is considered to be phosphorus-limited. This assumption is based mainly on very high inorganic N:P ratios, and the important organic nutrient pool has largely not been considered. Further information is needed in order to understand the complex nutrient dynamics, which depend on biologically mediated uptake/regeneration processes, physical forcing and freshwater nutrient input.

2.2. Site description

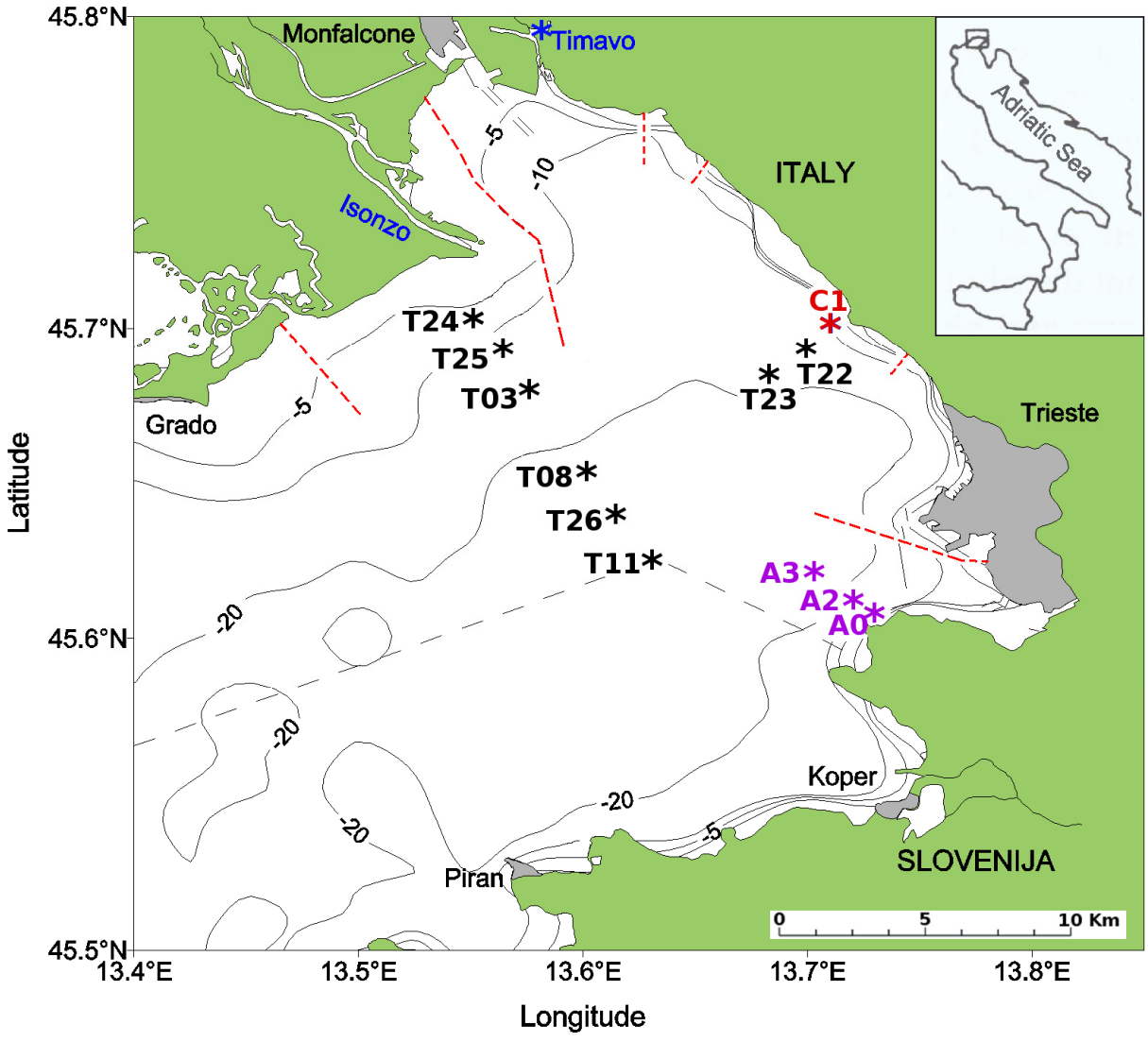

Fig.1. The Gulf of Trieste and the position of hydrographic stations

The Gulf of Trieste is the northernmost and shallowest part of the Adriatic Sea; it is limited in size (20 x 20km), with an average depth of about 17m (max depth 24m in its southern part) and a volume about 9.5km^3 (Olivotti et al. 1986). The Gulf's peculiar geomorphologic and hydrologic conditions make it prone to the accumulation of pollutants, since it is an elongated, sheltered bay with reduced hydrodynamism (Solis-Weiss et al. 2004). The hydrological characteristics are affected by strong thermal fluctuations between winter and summer. The temperature shows a regular annual pattern from a winter minima of about 6°C to a summer maxima >25°C (Cardin and Celio 1997). The water column is homogeneous from autumn to early spring because of the cooling and mixing effects of cold winds. The general circulation of the surface layer is strongly dependent on wind direction, rotating clockwise or counter clockwise according to easterly or westerly winds. In calm weather, tidal currents drive the same water mass forward and backward for about one kilometer (Malačič 1991), while they can be overlooked in the presence of strong winds when drift currents are dominant. In particular the Gulf is affected by two dominant winds: Bora (ENE) and Scirocco (SE). During Bora storms wind speeds can reach more than 30 ms^{-1}, producing a water outflow from the Gulf at the surface, an inflow at depth and strong vertical mixing (Mosetti and Mosetti 1990). Numerical studies indicate that a time interval of 2 days is long enough for the wind to homogenize the water column and to determine water renewal in the gulf (Querin et al. 2007). In late spring and summer the water column is characterized by a strong thermal stratification with a temperature gradient of about 10-12°C/20m (Celio et al. 2006).

The Gulf is mostly controlled by pulsed external inputs which determine a high variability of plankton communities (Fonda Umani et al. 2007). Freshwater inputs to the Gulf of Trieste show a high inter annual variability (Malej et al. 1995) affecting the surface salinity values, which normally range from 32 to 38psu through out the year (Celio et al. 2002). Isonzo River is the major source of land-born nutrients in the Gulf of Trieste, in particular because of nitrate leaching from agricultural soils of the region (Reisenhofer et al. 1996, Cantoni et al. 2003). It has an alpine hydrological regime with two flow rate minima (winter and summer) and two maxima (spring and autumn); Isonzo can reach a maximum discharge >1500 m^{3}s^{-1} and according to Olivotti et al. (1986), the mean annual flow rate is 80-110 m^{3}s^{-1}. However, a recent study on the Isonzo river discharge shows that in the period 1998-2005 it has a different discharge pattern, where the seasonal cycle is less definite and the annual mean flow rate is remarkably lower at about 60 m^{3}s^{-1} (Comici and Bussani 2007). This river is about 140 km long and flows through Western Slovenia and North-Eastern Italy. Its source lies in the Trenta valley in the Julian Alps of Slovenia at around 1100 meters of altitude. The drainage basin covers 3452 km^2, of which 1115 km^2 is in Italian territory (Autorità di bacino dei fiumi Isonzo, Livenza, Piave, Brenta-Bacchiglione, 2004), entering the Adriatic Sea close to the Italian city of Monfalcone.

Isonzo River represents the main freshwater source of the Gulf. However, many other small rivers and torrents like Timavo River, Rosandra and Ospo torrents in the Italian territory and Rižana and Dragonja Rivers in the Slovenian territory flow into the Gulf. Timavo River has a larger discharge

compared to the others and is 89km in length, 38km of which it flows underneath the Slovenian and Italian Karst, draining the karstic water. Its mean discharge for the years 2001-2007 was about 26.73 m^3s^{-1} with a maxima of about 144 m^3s^{-1} (ACEGAS-APS S.p.A.). This water is affected by the percolation waters that run through the karstic cracks and pores and drain organic anthropogenic pollutants of villages and farms (Olivotti et al. 1986). At the village of Škocjan it disappears underground through the Škocjan Caves and resurges later as the Italian Timavo River. After only 2km this river ends in a canal of Monfalcone harbor.

Treated sewage water is discharged into the Gulf by submarine pipelines: the most important coming from the two major cities in the area, Trieste and Monfalcone. The Servola (Trieste) sewage disposal plant is the most important sewage plant discharging water to the Gulf. Since 1992, its primary treatment has been based on chemical precipitation (Novelli 1996). It catches urban wastewaters and runoff corresponding to about 220.000 Equivalent Inhabitants and discharges the wastewaters in the Gulf of Trieste at the depth of 22 meters, through an underwater pipeline 7.5 km in length. The release of wastewaters in the water column occurs through 600 diffusers placed in the last section of the pipeline which is 1.5 km in length, and the average flow rate of wastewaters discharged by this underwater pipeline is 1.39 m^3s^{-1} (Cozzi et al. 2008). Submarine wastewater ducts and pipelines are shown in Fig.1 in red dotted color.

The Gulf sustains relevant shell-fish production (on average 4000 tons/year harvested by shell-fish farming) and fish production (886 tons fished in 2000) (Orel and Zamboni 2003). Local shell-fish harvesting is occasionally blocked by noxious blooms of HAB species (Cabrini et al. 2001) and hypoxic events in bottom waters in late summers have been reported several times (Stachowitsch 1984, Orel et al. 1986, Covelli et al. 1999). The trophic state of the Gulf has shown a progressive lowering in the last two decades (Paoli et al. 2006), with seasonal shifts from oligotrophic to mesotrophic status and is generally characterized by very high inorganic N:P ratios.

Fig. 2: Satellite image of Isonzo River plume spreading during high outflow (GOS ISAC CNR).

2.3. Spatial distribution and temporal variation of inorganic nutrients on nine stations (2004-2008)

2.3.1. Introduction

From January 2004 to February 2007, seawater samples were monthly taken at nine stations (T24, T25, T03, T08, T26, T11, C1, T22, T23) located in the Gulf of Trieste (Fig.1). Water samples were collected using a 5L Niskin bottles at three depths along the water column: surface (1m), intermediate depth and bottom. At the coastal station C1, samples were collected at four depths (surface, 5m, 10m, bottom) and the sampling project continued until December 2008.

This research was carried out under the auspices of INTERREG II and III (Italia-Slovenia) initiative, in the framework of projects "Studio dello stato trofico e delle anomalie del sistema Alto Adriatico" and EcoMAdr (Ecologia del Mar Adriatico), and with the support of V.E.C.T.O.R. (VulnErabilita' delle Coste e degli ecosistemi italiani ai cambiamenti climaTici e loro ruolO nei cicli del caRbonio mediterraneo) programme.

2.3.2. Methods

A total of 1070 samples were collected and nine environmental parameters were analyzed: N-NH_4, N-NO_2, N-NO_3, P-PO_4, SiO_2, Dissolved Organic Nitrogen (DON), Dissolved Organic Phosphorus (DOP), Particulate Nitrogen (PN) and Particulate Phosphorus (PP).

For inorganic nutrients and DON and DOP determinations, water samples were filtered on GF/F glass fiber filters (0.7µm nominal pore size, 47mm diameter, Whatman International Ltd). Inorganic nutrient analyses were conducted at room temperature on a five-channel Bran+Luebbe Autoanalyser3 Continuous Flow Analyser (Bran+Luebbe, Norderstedt, Germany), using standard procedures (Bran+Luebbe 2003a,b,c,d,e and references therein). The efficiency of the system was checked before and after sample analyses by replicating calibration standards. DOP and DON concentrations were determined using a UV+H_2O_2 oxidation procedure (Walsh 1989). After the step of oxidation, total dissolved nitrogen and phosphorus were determined with the same automated colorimetric methods used for nitrate and reactive phosphorus. The concentrations of DON and DOP were calculated as the difference between total dissolved nitrogen and phosphorus and the ambient concentrations of dissolved inorganic nitrogen, calculated as N-NH_4+N-NO_2+N-NO_3 (DIN) and P-PO_4, respectively.

For Particulate Nitrogen (PN) determination, 250mL of sample were filtered on pre-combusted GF/F glass fiber filter (25mm diameter, Whatman International Ltd) and determined by high temperature oxidation according to Sharp (1974) on a Perkin Elmer 2400 CHNS/O analyzer. For Particulate Phosphorus (PP) determination, water sample (1L) was filtered on pre-combusted GF/F glass fiber filter (25mm diameter, Whatman International Ltd). After high temperature combustion (480°C) in a muffle-oven for 2.5h, PP was extracted from the filter by acid hydrolysis using 1M HCl solution for 24h and subsequently analyzed as P-PO_4 (Solorzano and Sharp 1980).

At each sampling station, a CTD profile was recorded using a Seabird19 Plus multiparametric probe, which was calibrated every 6 months. Salinity was computed, according to the UNESCO formula for salinity determination (UNESCO 1978), from measurements of hydrostatic pressure, temperature and conductivity.

For chlorophyll *a* determination, aliquots of seawater (1L) were filtered through GF/F glass fiber filter (47mm diameter, Whatman International Ltd). Filters were immediately frozen (-20°C) until analyses. Pigments were extracted overnight in the dark at 4°C with 90% acetone from the homogenate filter and the concentrations were spectrofluorometrically determined following the procedures described by Lorenzen and Jeffrey (1980) using a Perkin Elmer LS50B spectrofluorometer (450nm excitation and 665nm emission wavelengths).

2.3.3. Results

2.3.3.1. Main hydrological features of each station

Descriptive statistics of the main hydrological features of each station are summarized in Table 1., which are organized so they start from the northernmost sampling station (T24), nearest Isonzo River mouth, going southward to station T11, and then from coastal station C1 to station T23. The tables are based on the whole dataset (all sampling depths together).

Salinity [psu]

	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	36.79	37.75	38.04	38.27	38.30	38.31	38.35	38.39	38.43
Min	26.14	22.43	28.03	32.11	33.48	31.97	32.41	33.30	33.29
Median	34.11	34.68	36.45	37.15	37.15	37.17	37.27	37.31	37.30
Average	33.36	33.82	35.28	36.70	36.83	36.84	37.06	36.96	36.81
Std.Dev.	2.49	3.54	2.47	1.34	1.13	1.25	1.12	1.18	1.27

Temperature [°C]

	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	25.66	25.83	26.20	26.03	26.39	26.69	26.17	26.06	26.03
Min	7.53	7.54	7.50	8.06	7.83	8.04	6.82	7.02	7.28
Median	15.76	15.78	16.40	17.23	17.20	16.87	17.20	17.40	17.42
Average	16.60	16.91	16.90	17.03	17.20	17.04	16.15	16.63	16.85
Std.Dev.	6.39	6.47	6.40	6.24	6.08	5.97	6.26	6.29	6.28

O_2 [mL/L]

	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	7.12	7.18	7.36	6.95	6.80	6.81	6.79	6.76	6.83
Min	4.93	4.86	4.82	4.76	4.84	4.20	4.50	4.59	4.52
Median	5.79	5.84	5.68	5.57	5.57	5.54	5.56	5.60	5.58
Average	5.94	5.87	5.81	5.68	5.65	5.62	5.57	5.64	5.62
Std.Dev.	0.68	0.68	0.69	0.64	0.62	0.68	0.59	0.65	0.66

Secchi depth [m]

	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	8.6	12.4	14.8	18.4	19.4	20.0	16.4	18.6	15.9
Min	0.7	2.0	3.2	5.6	5.6	6.0	3.1	3.2	3.2
Median	4.9	7.5	7.6	9.4	10.0	9.5	9.4	8.7	9.0
Average	4.8	7.5	8.5	9.8	10.4	10.7	9.8	9.6	9.5
Std.Dev.	2.2	3.0	3.2	3.4	3.7	3.7	2.7	3.6	3.3

Chl *a* [µg/L]

	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	3.00	2.48	1.96	2.38	3.09	2.47	2.28	3.44	3.30
Min	0.09	0.07	0.10	0.08	0.06	0.07	0.10	0.09	0.10
Median	0.59	0.50	0.46	0.45	0.58	0.40	0.64	0.49	0.55
Average	0.84	0.62	0.70	0.68	0.70	0.61	0.73	0.71	0.79
Std.Dev.	0.74	0.52	0.52	0.64	0.64	0.55	0.44	0.68	0.70

Table 1

No hypoxic conditions (<1.4mL O_2 L^{-1}) were evidenced in the Gulf. Oxygen concentration ranged from 4.20 to 7.36mL/L^{-1}.

Salinity values ranged between 22.43 and 38.43. The lowest value was reached at station T25 in May 2004, but considering the average values, the station T24 resulted more influenced by freshwater inputs.

The lowest water temperature was recorded at station C1 in February 2004, while the maximum was registered at station T11. The lowest value of Secchi depth was registered at station T24 in January 2004.

2.3.3.1.2. Isonzo River discharge (2004-2008)

Monthly mean Isonzo River discharge is showed in Fig. 3. Lowest discharge in the five years of monitoring were generally recorded in the summers; in 2004 lowest discharge was recorded in August (13.14 m^3s^{-1}), however in 2005 very low mean discharge to place in February (1.13 m^3s^{-1}), but also in June (4.34 m^3s^{-1}). In 2006, July (0.62 m^3s^{-1}) and September (9.41 m^3s^{-1}) were the "driest" months. In 2007 a very low mean discharge was recorded in August (1.66 m^3s^{-1}) while the lowest in 2008 was in September (6.68 m^3s^{-1}). The highest (>90 m^3s^{-1}) monthly mean river discharge was in 2004 recorded in April (96.74 m^3s^{-1}), in May (127.7 m^3s^{-1}), in October (192.08 m^3s^{-1}) and in November (136.89 m^3s^{-1}). In 2005, highest monthly mean river discharge were recorded in April (107.67 m^3s^{-1}) and December

(97.60 m^3s^{-1}). In 2006, in March (124.65 m^3s^{-1}) and December (97.36 m^3s^{-1}), and in 2007 in February (104.62 m^3s^{-1}). In 2008 Isonzo River discharge was very high (Tab. 2), with highest mean discharge in January (94.19), April (153.06) , May (108.65), November (135.39) and December 2008 (327.12 m^3s^{-1}), which was the month with highest mean discharge in the four years of study.

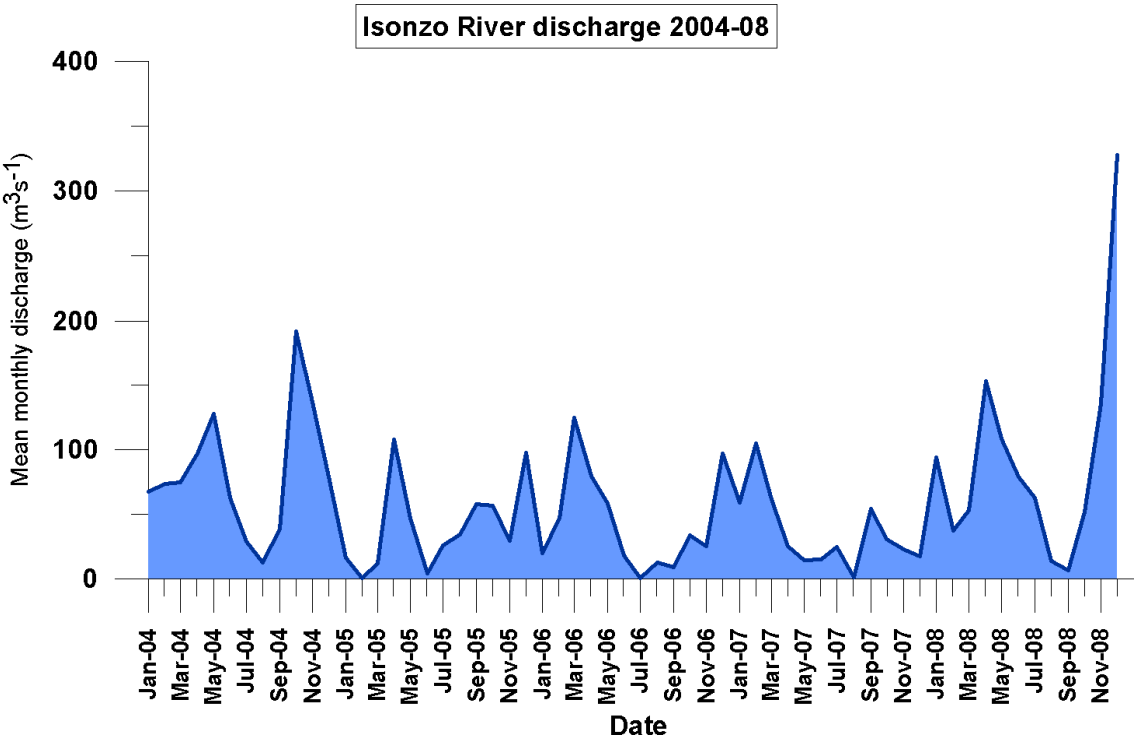

Fig. 3

Descriptive statistics of the mean monthly river discharge [m^3s^{-1}] are summerised in Tab. 2. Overall, year 2005, 2006 and 2007 were on average the years with the lowest river outflow, remarkable lower than the mean annual flow rates found by Olivotti et al. 1986 (80-110 m^3s^{-1}).

Isonzo River					
	2004	**2005**	**2006**	**2007**	**2008**
Max	192.08	107.67	124.65	104.62	327.12
Min	13.14	1.13	0.62	1.66	6.68
Median	74.13	32.27	29.70	25.24	70.70
Average	82.73	41.03	44.01	36.13	93.57
Std.Dev.	50.00	34.32	38.81	28.70	86.15

Table 2

2.3.3.2. Spatial distribution and temporal variation of dissolved inorganic nutrients

Descriptive statistics of the spatial distribution of dissolved inorganic nutrients, measured in the Gulf of Trieste in the period January 2004 - February 2007, are summarized in the following tables, where the sampling stations are organized so they start from the northernmost station (T24), nearest

Isonzo River mouth, going southward to station T11, and then from coastal station C1 to station T23. The general temporal variations in dissolved inorganic nutrients are best noticeable in box plots. Median values are stronger and more robust appraisers of central tendency than average values (Rousseeuw 1991). A colored line between monthly median values has been added in order to aid visualization. As for the tables, these plots are based on the whole dataset (all sampling depths together).

2.3.3.2.1. Ammonium

In Table 3 the descriptive statistics for the spatial distribution of $N\text{-}NH_4$ concentration during the investigation period is presented. The median concentration resulted to be rather similar, around 1µM, at all considered stations.

$N\text{-}NH_4$ µM									
	T24	**T25**	**T03**	**T08**	**T26**	**T11**	**C1**	**T22**	**T23**
Max	3.68	3.04	2.93	5.53	6.57	4.71	9.31	4.08	3.46
Min	0.09	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Median	1.06	1.02	0.90	1.04	0.82	1.20	0.92	0.99	1.03
Average	1.24	1.03	1.01	1.23	1.13	1.23	1.03	1.22	1.17
Std.Dev.	0.76	0.60	0.62	0.99	1.04	0.87	0.80	0.88	0.78

Table 3.

Temporal variations in ammonium concentrations are showed in Figure 4.

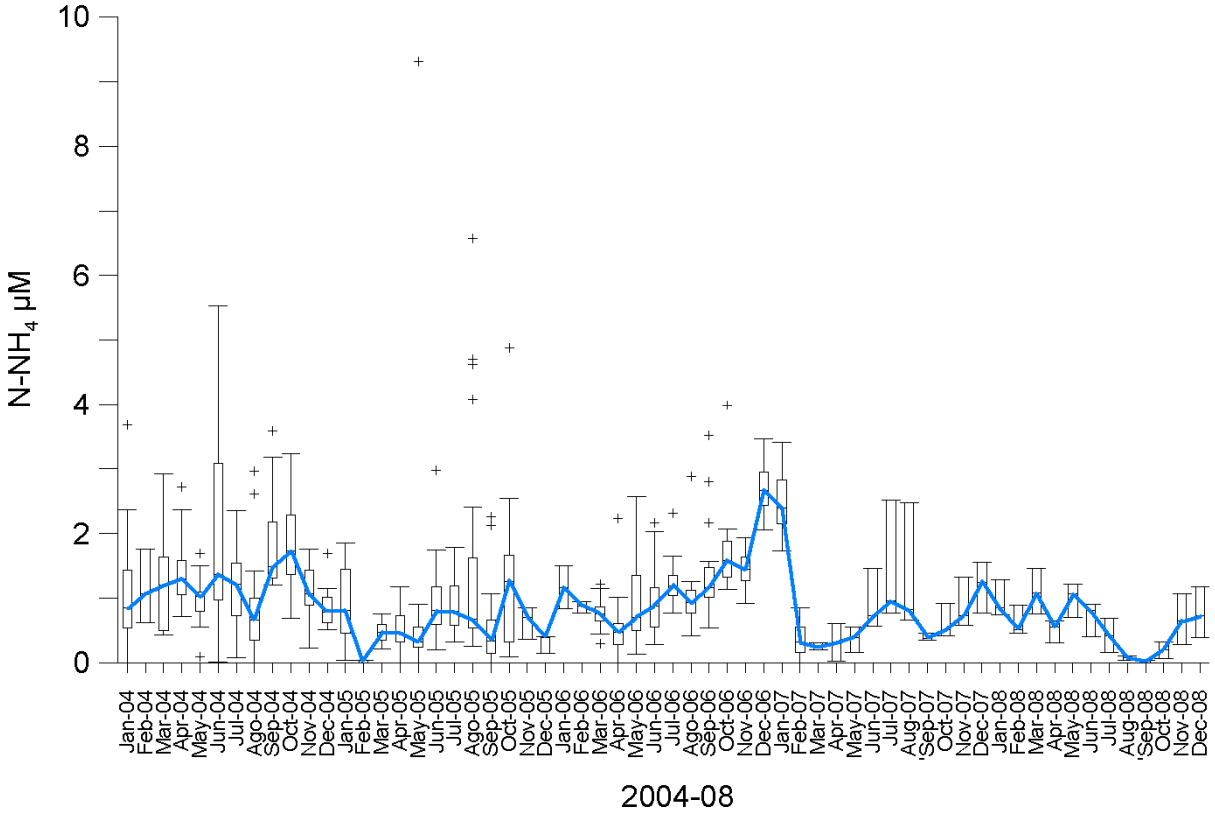

Fig.4

No clear annual or seasonal trend could be noticed in the period of study. The yearly median value for 2008 (0.64µM) was similar compared to that of 2007 (0.66µM) and 2005 (0.58µM), but lower than that of 2004 (1.10µM) and 2006 (1.10µM). However care should be taken when comparing annual median values, because, from March 2007, sampling was carried out only on station C1. Overall highest ammonium concentration (9.31µM) was recorded on coastal station C1 near surface (1m) in May 2005. Very low ammonium concentrations were recorded on the same station in February 2005 and in August and September 2008.

2.3.3.2.2. Nitrite

Table 4 reports the descriptive statistics for the spatial distribution of nitrites in the period of investigation. Overall highest nitrite concentration (3.39µM) was evidenced on station C1 near the bottom (15m) in November 2004. The median concentration of nitrite for the period of investigation resulted to be rather similar on all stations, around 0.09µM.

$N\text{-}NO_2$ µM									
	T24	**T25**	**T03**	**T08**	**T26**	**T11**	**C1**	**T22**	**T23**
Max	1.65	1.70	2.03	1.74	2.11	1.90	3.39	1.01	0.78
Min	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Median	0.10	0.09	0.08	0.09	0.07	0.09	0.10	0.10	0.08
Average	0.24	0.23	0.25	0.23	0.26	0.26	0.23	0.17	0.15
Std.Dev.	0.35	0.36	0.40	0.36	0.42	0.41	0.36	0.21	0.17

Table 4

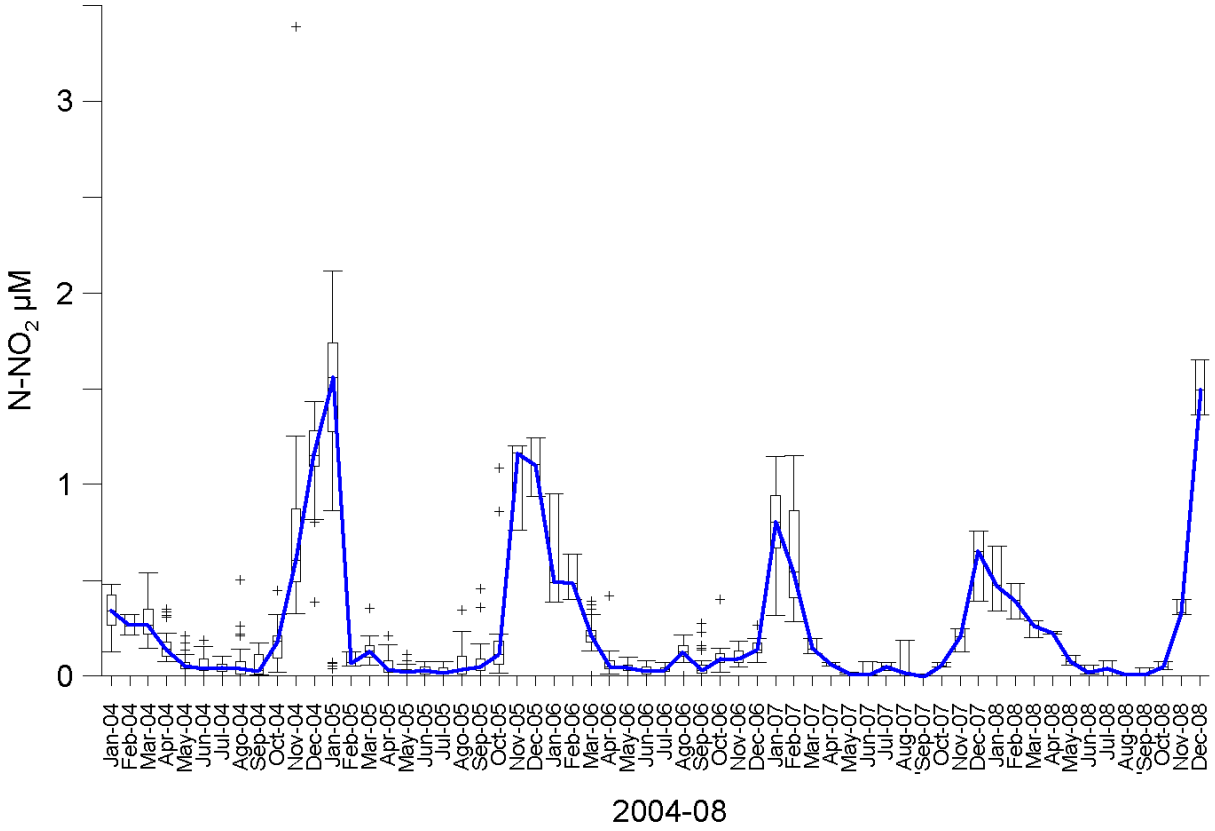

Fig. 5

The very clear seasonal variation could be noticed, with relatively high late autumn and winter concentrations and very low values in all summer periods. The median nitrite value for year 2004 (0.14µM) resulted slightly higher than of 2005 (0.05µM) and of 2006 (0.08µM), but lower than that of 2007 (0.46µM) and similar to 2008 (0.16µM).

2.3.3.2.3. Nitrate

The median concentration of nitrate for the period of investigation resulted to vary between the stations, and the one with the highest nitrate median value, calculated on the whole sampling period, resulted to be the station nearest the Isonzo river mouth, station T24 (Tab. 5). However, also the median nitrate value at coastal station C1 resulted to be higher than the ones registered at station T22 and T23.

$N\text{-}NO_3$ µM

	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	18.91	34.26	21.01	7.06	7.02	6.96	11.96	12.54	9.90
Min	0.01	0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	0.04	0.00
Median	1.82	1.27	0.89	0.65	0.65	0.84	0.85	0.70	0.64
Average	3.23	2.99	2.16	1.26	1.35	1.31	1.42	1.29	1.19
Std.Dev.	3.78	4.99	3.29	1.57	1.72	1.50	1.90	1.99	1.61

Table 5

Overall highest nitrate concentration (34.26µM) was evidenced at station T25 on surface in May

2004, but in the same period a relatively high nitrate concentration (15.96 µM) was detected also at station T24. During the all years of sampling, the nitrates remained the largest fraction (about 50%) of the total dissolved inorganic nitrogen (DIN) pool, and its seasonal variation followed that of the nitrites, with the highest median values in winters and the lowest ones in summers (Fig. 6).

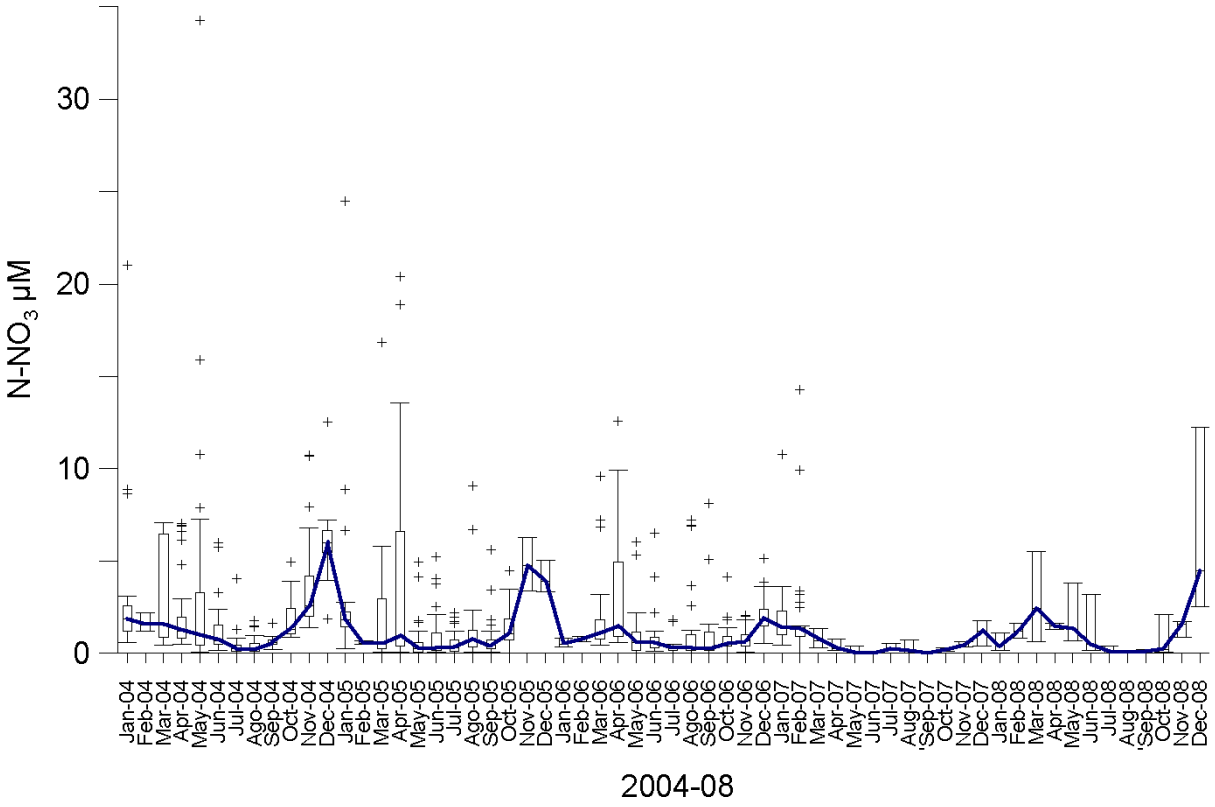

Fig.6

In March 2004 surface nitrate concentrations reached high values at all the stations in the Gulf. Surface layer concentrations were rather high in all northernmost stations in April 2005, possibly due to high Isonzo River discharge in this month. The same situation occurred in April 2006. Median nitrate value for year 2004 (1.14µM) was higher than in 2005 (0.61µM) and in 2006 (0.67µM), and the highest overall nitrate concentration (34.26µM) was evidenced at station T25 on surface in May 2004.

2.3.3.2.4. Phosphate

Table 6 reports the descriptive statistics for the spatial distribution of phosphate in the period of investigation. The median value of phosphate concentration for the period of investigation resulted to be similar at all stations, around 0.05µM, and without any spatial trend. The median phosphate value of 2004 (0.06µM) resulted to be similar to that of 2005 (0.05µM), but slightly higher than of 2006 (0.04µM). The median value of 2007 was 0.05µM, while that of 2008 was 0.06µM.

Highest overall phosphate value (0.50µM) was recorded at station T22 in January 2007 near the

bottom (15m).

P-PO$_4$ µM	**T24**	**T25**	**T03**	**T08**	**T26**	**T11**	**C1**	**T22**	**T23**
Max	0.22	0.17	0.46	0.26	0.30	0.22	0.28	0.50	0.35
Min	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Median	0.05	0.05	0.05	0.05	0.04	0.05	0.06	0.06	0.05
Average	0.05	0.05	0.06	0.06	0.06	0.06	0.06	0.07	0.05
Std.Dev.	0.04	0.04	0.06	0.05	0.05	0.04	0.04	0.07	0.05

Table 6.

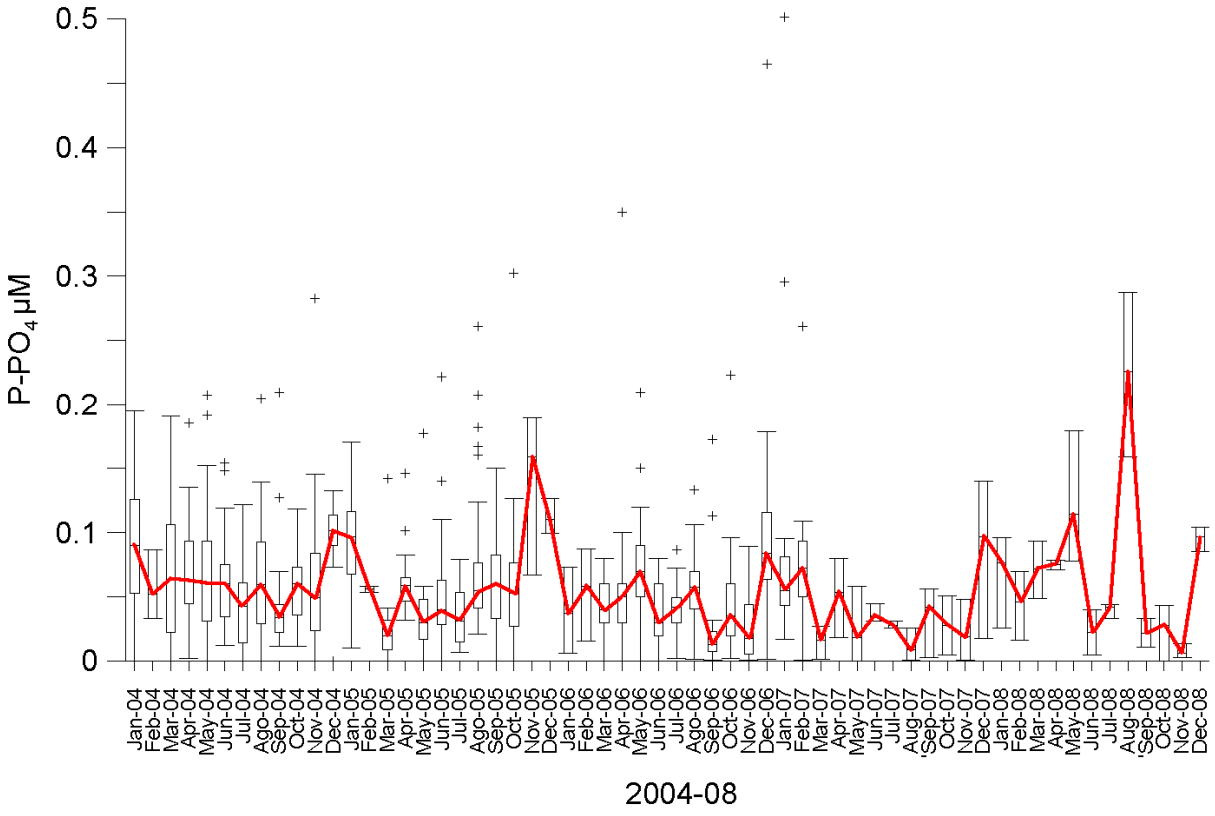

Fig. 7

Phosphate concentrations were always low in 2006, with September concentrations near the analytical detection limit (0.02µM). Maximum overall phosphate concentration (0.50µM) was evidenced in January 2007 on station T22, near the bottom (18m). No clear seasonal trend could be evidenced, even though slightly higher median values were found in the winter months.

2.3.3.2.5. Silicate

Silicate is essential for the frustules of diatoms and its depletion inhibits the cell division and eventually suppresses the metabolic activity of the cell (Levinton 1995). Growth of diatoms depends

on the presence of dissolved silicate, whereas growth of non-diatom phytoplankton does not. When silicate concentrations become low, other types of algae that do not require silicate can dominate algal community composition and decrease the relative importance of diatoms in phytoplankton communities (Conley et al. 1993). Table 6 reports the descriptive statistics for the spatial distribution of silicate in the period of investigation.

SiO_2 µM									
	T24	**T25**	**T03**	**T08**	**T26**	**T11**	**C1**	**T22**	**T23**
Max	10.90	15.18	11.76	16.70	17.44	16.10	10.80	13.45	11.32
Min	0.28	0.20	0.11	< 0.02	0.15	0.24	< 0.02	< 0.02	< 0.02
Median	2.94	2.44	2.19	2.44	2.38	2.36	2.26	2.56	2.15
Average	3.27	3.01	2.74	2.80	2.88	2.75	2.60	2.72	2.40
Std.Dev.	2.09	2.35	2.13	2.25	2.60	2.26	1.60	2.08	1.66

Table 7.

Maximum silicate concentration (17.44µM) was evidenced in October 2005 on station T26, near the bottom (26m). Considering the spatial distribution of silicate, the highest median value of silicate was evidenced, as for nitrates, on station T24, confirming the importance of fresh water outflow from Isonzo River.

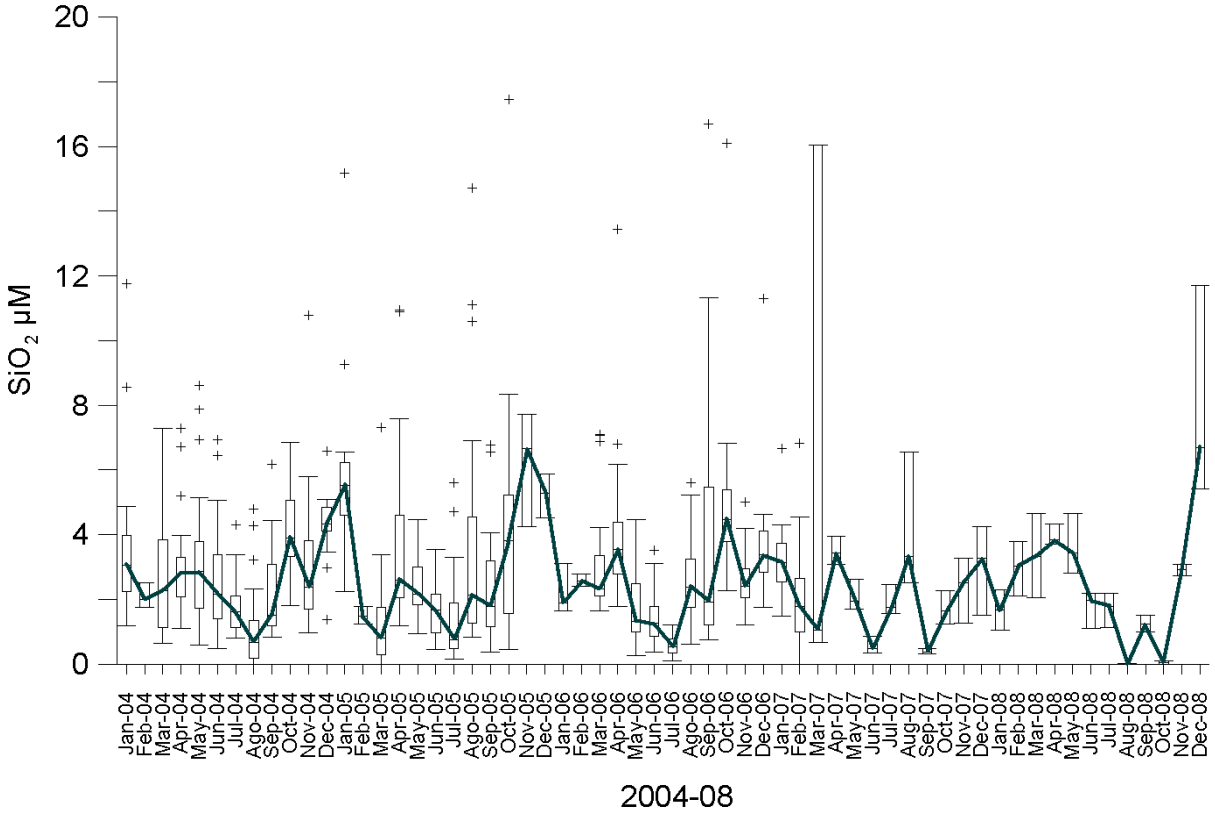

Fig. 8

From 2004 to 2008, the lowest silicate concentrations were found in summers and the highest in winters. The lowest median value was reached in August 2008 (0.01µM) and in October 2008 (0.05µM). The median values calculated on year 2004 (2.40µM), 2005 (2.14µM) and 2006 (2.40µM), 2007 (2.29µM) and 2008 (2.25µM) resulted very similar.

2.3.3.3 Spatial distribution and temporal variation of dissolved organic nutrients

2.3.3.3.1 Dissolved Organic Nitrogen (DON)

Table 8 reports the statistics for the spatial distribution of DON in the period of investigation. Very high DON concentrations were found in September 2005 at station C1 along the water column (5, 10 and 15m) and at surface of station T08 and T25 in October 2005.
The highest median DON value was evidenced at station T24, as for nitrates and silicates.

DON µM									
	T24	**T25**	**T03**	**T08**	**T26**	**T11**	**C1**	**T22**	**T23**
Max	46.45	38.58	32.93	117.27	90.75	61.99	126.47	37.10	24.69
Min	0.29	0.09	0.17	0.11	0.63	0.37	0.29	0.44	0.30
Median	11.04	9.29	8.54	10.32	10.33	9.39	9.89	8.96	9.54
Average	12.87	10.90	8.92	14.10	13.04	11.20	12.50	10.08	9.88
Std.Dev.	9.28	7.31	5.48	16.37	12.62	9.26	13.16	6.31	5.50

Table 8.

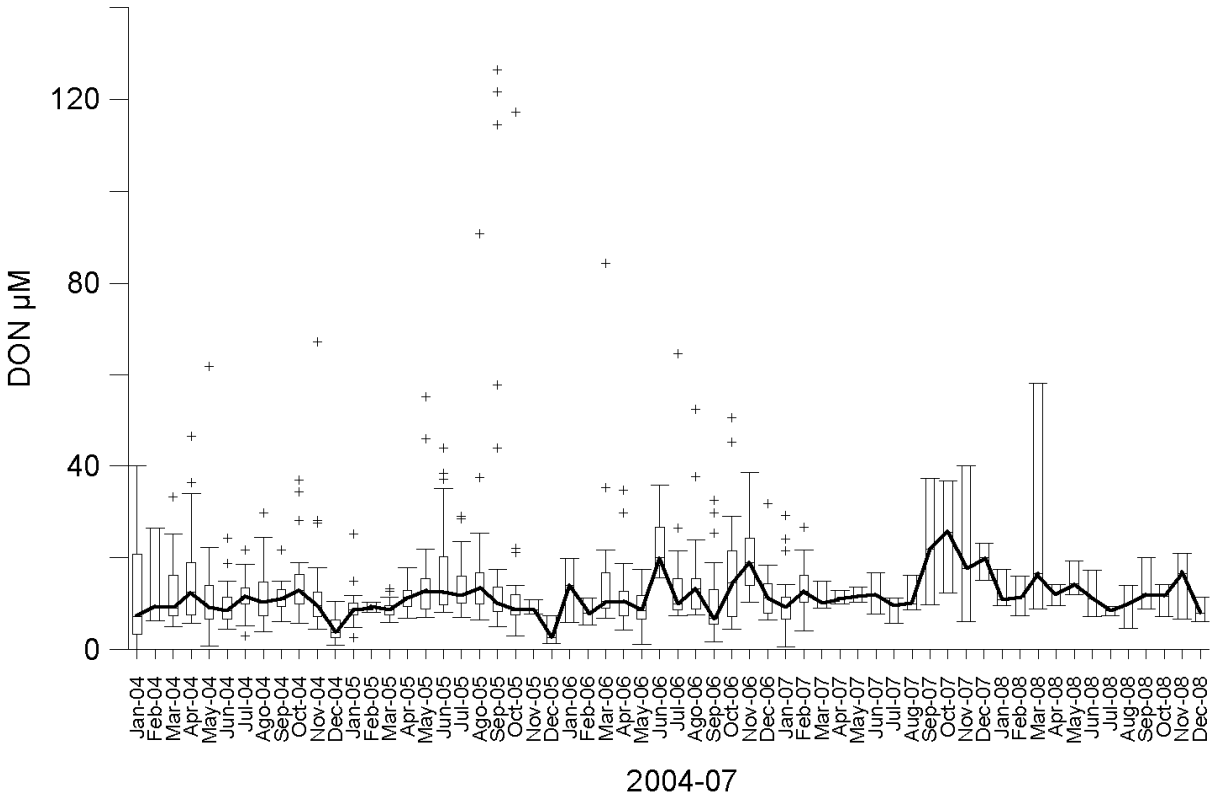

Fig. 9

The median value of DON in 2004 (9.66µM) was similar to that of 2005 (10.49µM), while for 2006, the median nitrate value resulted somewhat lower (7.58µM). On the other hand, the 2007 median value (11.29µM) and 2008 value (11.21µM) were very similar. A clear visible yearly trend is noticeable in the first two years of sampling, with lowest concentrations in winter and highest in summer. DON remained the most conspicuous fraction of the total nitrogen pool in the investigated period. In 2004, DON constituted on average 65% of the total N pool (PN 15% and DIN about 20%); in 2005 approximately 72% (PN 16% and DIN 12%) and in 2006 about 56% (PN 28% and DIN 16%).

2.3.3.3.2 Dissolved Organic Phosphorus (DOP)

Table 9 reports the descriptive statistics for the spatial distribution of DOP in the period of investigation.

DOP µM									
	T24	**T25**	**T03**	**T08**	**T26**	**T11**	**C1**	**T22**	**T23**
Max	5.07	3.50	4.14	3.47	2.18	3.18	6.75	2.43	1.64
Min	< 0.02	0.02	0.05	< 0.02	< 0.02	0.03	0.04	< 0.02	< 0.02
Median	0.32	0.37	0.45	0.48	0.35	0.37	0.43	0.31	0.37
Average	0.54	0.53	0.67	0.73	0.53	0.62	0.70	0.52	0.43
Std.Dev.	0.75	0.51	0.75	0.76	0.51	0.67	0.78	0.46	0.33

Table 9

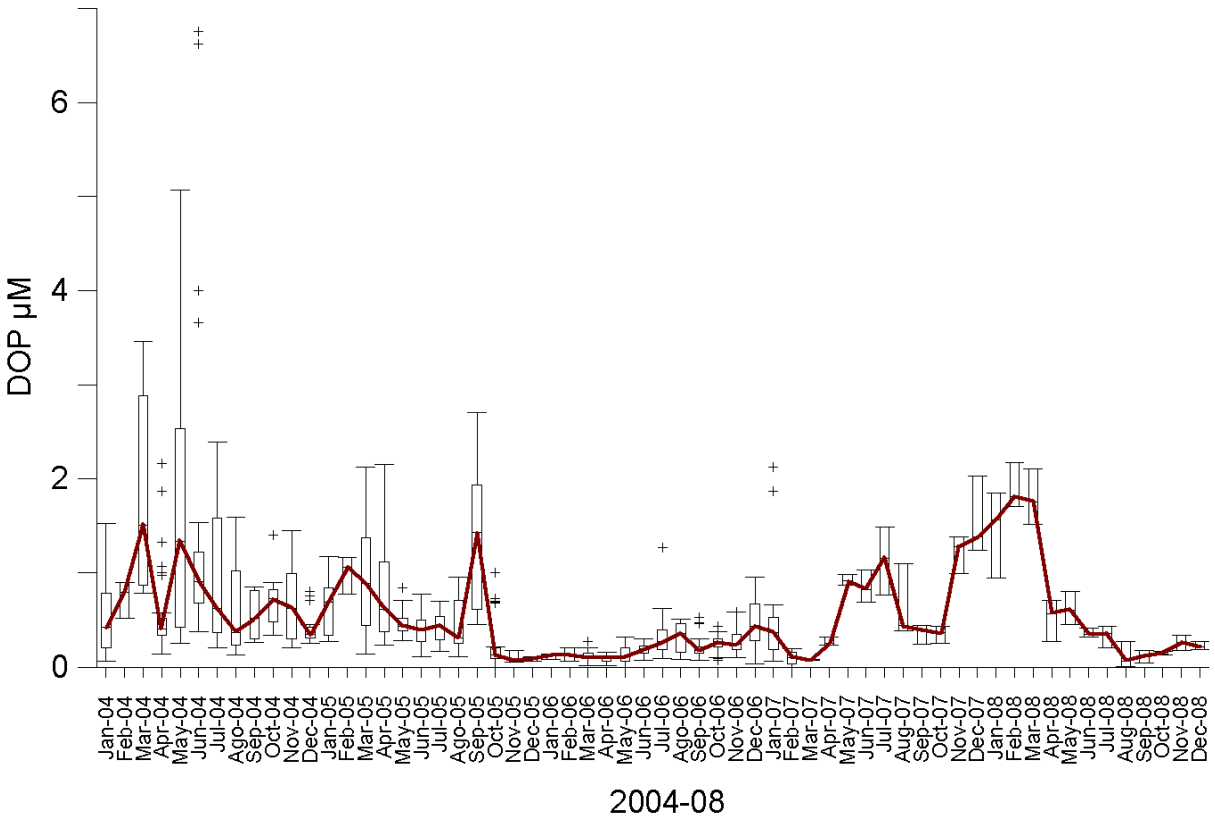

Fig. 10

Interestingly, in 2006, DOP concentrations varied less compared to previous years with generally lower concentrations. A very transparent water column was also recorded in 2006 and especially in summer water transparency was very high (Secchi disc depth reaching the bottom in many stations), while freshwater discharge from Isonzo River was very low.

The DOP remained the most conspicuous fraction of the total phosphorus pool in the years of monitoring. In 2004 DOP constituted on average 83% of the total phosphorus pool, (Particulate P 11% and DIP about 6%), and in 2005 about 75% (PP 18% and DIP 7%). In 2006 the particulate fraction (PP) got more important due to relatively low DOP content which constituted about 56% (PP about 33% and DIP 11%). In 2007, DOP constituted on average 78% of the total phosphorus pool (PP 12%, DIP 10%), and curiously, in 2008 DOP also 78% (PP 13%, DIP 9%).

2.3.3.4. Spatial and temporal Particulate Nitrogen (PN) and Phosphorus (PP) distribution

2.3.3.4.1. Particulate Nitrogen (PN)

The descriptive statistics for the spatial distribution of Particulate Nitrogen in the period of investigation is reported in Table 10. The station T24, located nearest the Isonzo River mouth, reached

the highest median PN value. PN determinations did not carried out in the period from November 2005 to February 2006 and from March 2007 to December 2008.

The highest median value of PN was detected in 2006 (4.28 µM) and resulted higher than 2004 (2.66 µM) and 2005 (2.73 µM) values.

PN µM									
	T24	**T25**	**T03**	**T08**	**T26**	**T11**	**C1**	**T22**	**T23**
Max	13.63	8.00	11.63	9.61	23.45	11.09	10.15	12.61	12.43
Min	0.35	0.43	0.07	0.15	0.01	0.18	0.14	0.01	0.13
Median	3.44	3.09	2.56	2.90	2.70	3.01	2.77	3.08	3.22
Average	4.07	3.41	3.26	3.13	3.45	3.47	3.08	3.45	3.62
Std.Dev.	2.49	1.76	2.29	1.83	2.83	1.95	1.62	2.44	1.94

Table10

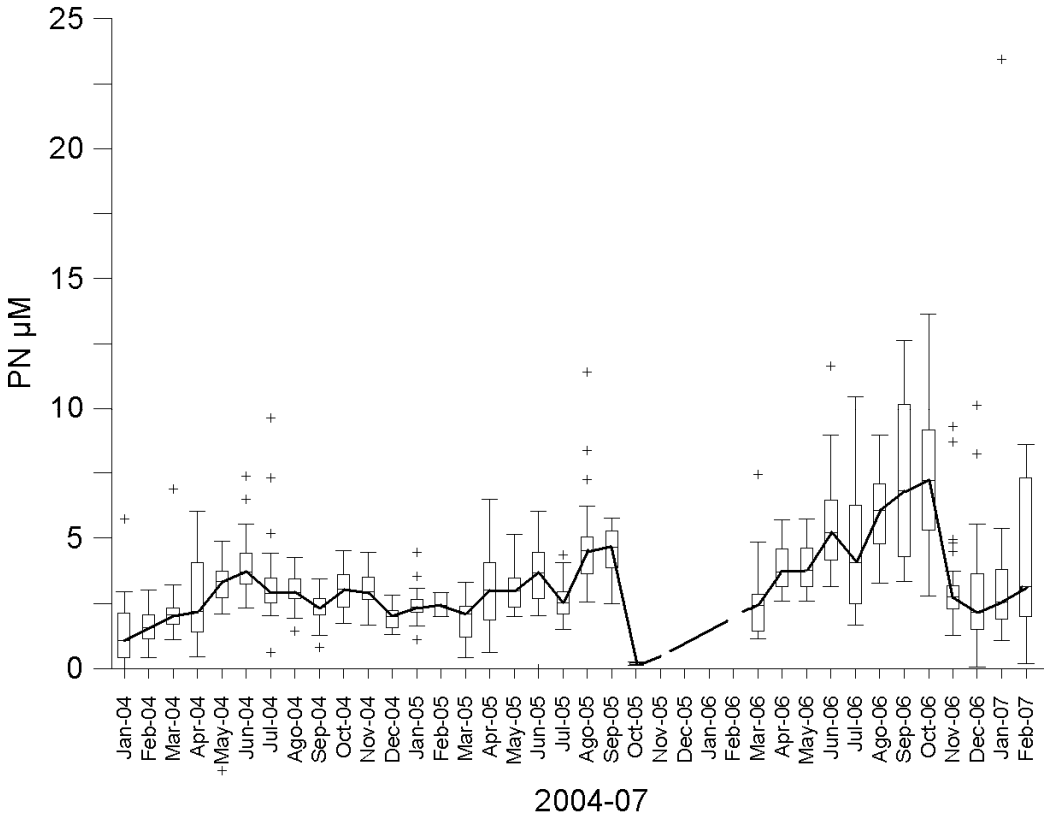

Fig. 11

No clear visible yearly trend was noticeable in the three years of sampling, but the lowest monthly median values were found in the winters.

2.3.3.4.2. Particulate Phosphorus (PP)

The descriptive statistics for the spatial distribution of PP in the period of investigation is reported in Table 11. The station with the highest median PP value resulted to be the station T24

nearest the Isonzo River mouth.

PP µM	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	4.45	0.36	0.40	0.32	0.32	0.40	1.01	0.40	0.52
Min	0.04	0.03	0.03	0.02	0.02	0.02	< 0.02	0.02	0.03
Median	0.16	0.14	0.12	0.11	0.11	0.11	0.11	0.11	0.11
Average	0.23	0.14	0.13	0.12	0.12	0.12	0.12	0.13	0.13
Std.Dev.	0.45	0.06	0.06	0.06	0.05	0.07	0.07	0.07	0.08

Table 11.

A very high PP concentration (4.45µM) was found at station T24 near the bottom(8m) in August 2005. In order to aid visualization of the monthly variations of PP, this value was omitted in Fig.12.

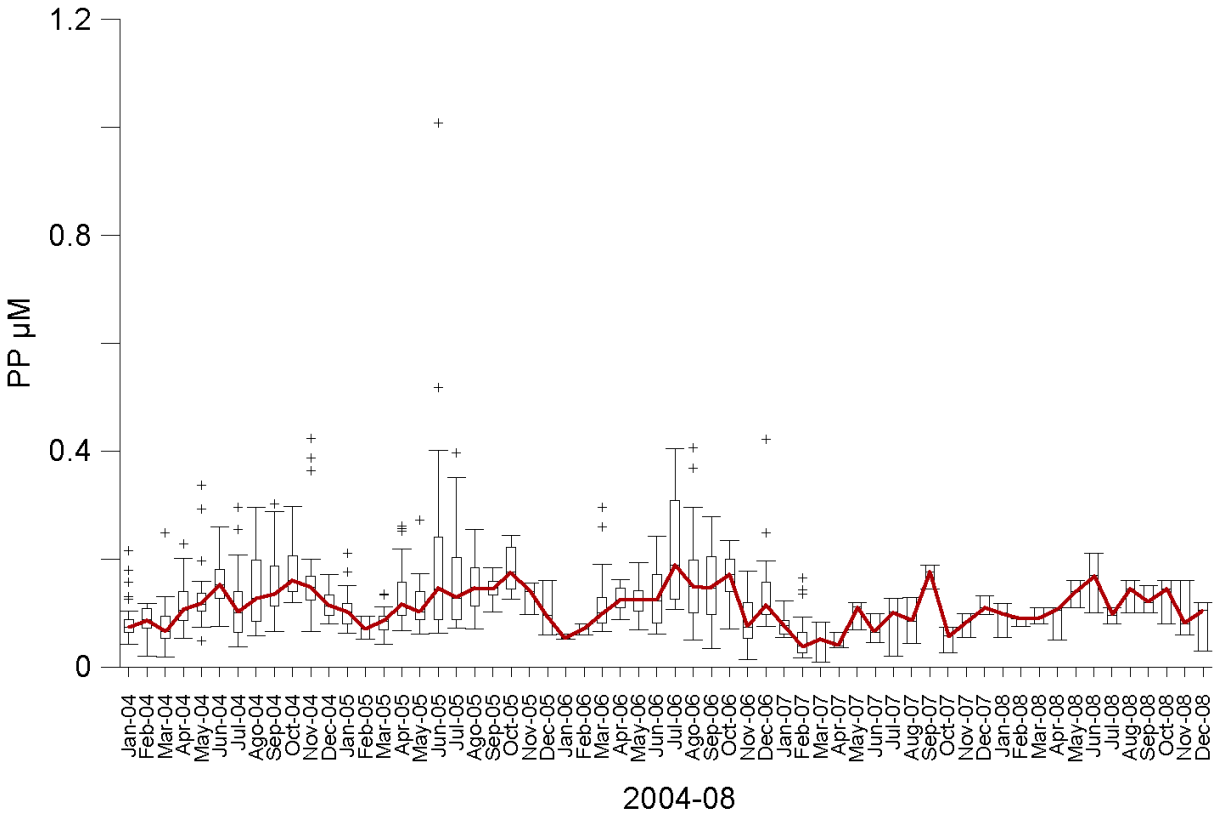

Fig. 12

The median values calculated on year 2004 (0.11µM), 2005 (0.12µM), 2006 (0.13 µM), 2007 (0.07µM) and 2008 (0.11µM) resulted very similar.

A clear visible yearly trend is noticeable in the four years of sampling, with highest monthly median values found around Octobers, and the lowest ones in the late winters.

2.3.3.5. Stoichiometric nutrient ratios

The descriptive statistics for the different nutrient ratios are reported in Table 12. Median

dissolved inorganic N:P ratios (DIN:DIP) and Si:DIP ratios resulted to be highest at station T24, while lowest median Si:DIN was evidenced at the same station, possibly due to high nitrate concentrations in Isonzo River waters.

Median inorganic Si:DIN ratio varied around the balanced ratio of 0.94 (Harrison et al. 1977) between the stations, possibly depending on fresh water outflow and/or phytoplankton uptake.

Median inorganic DIN and DIP ratios were well beyond the Redfield ratio of 16 at all stations. However, lower ratios were reached sporadically at all stations in "dry" periods characterized by high salinity values.

DIN:DIP

	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	5770	4953	609	2927	1270	2466	3466	2455	6421
Min	4.3	3.8	0.3	0.3	5.1	7.2	2.8	1.5	3.7
Median	86	66	44	46	41	47	40	39	46
Average	325	262	71	160	87	141	124	140	199
Std.Dev.	913	770	81	420	153	371	403	356	728

Si:DIP

	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	3461	4928	334	1638	2220	1296	4687	880	3092
Min	3.6	6.7	1.4	0.1	1.5	5.1	0.0	0.0	1.0
Median	60	55	46	47	49	48	44	45	43
Average	208	217	61	120	106	115	113	106	186
Std.Dev.	551	681	58	241	252	246	369	184	545

Si:DIN

	T24	T25	T03	T08	T26	T11	C1	T22	T23
Max	3.40	6.42	7.56	9.28	11.27	8.49	12.14	19.12	6.90
Min	0.18	0.19	0.24	0.09	0.28	0.17	0.00	0.00	0.00
Median	0.70	0.83	0.88	0.94	1.04	0.90	1.02	0.90	0.85
Average	0.89	1.04	1.18	1.27	1.39	1.24	1.39	1.58	1.21
Std.Dev.	0.60	0.83	1.08	1.15	1.38	1.24	1.38	2.41	1.01

Table 12.

2.3.3.6. Principal Component Analysis

Principal Component Analysis (PCA) based on r algorithm (correlation coefficient) was performed using MATEDIT software (Burba et al. 1992). The goal of the PCA was to reveal how different variables change in relation to each other, or how they are associated. The data matrix for PCA was constructed as follows: variables in rows and samplings dates in columns. From this data matrix a correlation coefficient matrix was calculated among rows. Correlation coefficients corresponding to 5% level of significance were considered and are evidenced in yellow in the cross-correlation tables, while correlation coefficients corresponding to 1% level of significance are reported

in cyan. Following variables were considered: Dissolved inorganic nutrients ($N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, $P\text{-}PO_4$, SiO_2), dissolved organic nutrients (DON, DOP), Particulate Nitrogen and Phosphorus (PN, PP), Chlorophyll *a*, dissolved oxygen (OXY), salinity (SAL), temperature (TEMP), wind intensity (WIND) and Secchi disc depth (SECCHI). Wind intensity was calculated as average of wind intensity on the sampling date and on the two days preceding the sampling date. Secchi disc depth was utilized as an indicator of water column transparency. The PCA was performed on each sampling station and sampling depth independently and the bi-plots are reported in Appendix. Two sampling depths were elaborated for each station; surface (1m) and near bottom (depth depending of local maximum depth). The cross-correlation tables are organized in a way, so they start from the northernmost station (T24) nearest Isonzo River mouth, going southward to station T11, and then from coastal station C1 to station T23.

T24:

In Table 13 is reported the correlation coefficients at each sampling depth.

T24 1m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,17	1													
PP	0,05	0,37	1												
N-NH4	0,01	0,09	0,10	1											
N-NO2	0,57	-0,04	0,00	0,14	1										
N-NO3	0,70	0,33	0,40	-0,17	0,35	1									
DON	-0,10	0,15	0,18	0,22	-0,27	-0,03	1								
PN	-0,39	-0,14	-0,03	-0,33	-0,26	-0,24	0,07	1							
SiO2	0,74	0,23	0,32	0,13	0,50	0,84	0,14	-0,31	1						
CHLa	-0,17	0,07	0,11	-0,28	-0,02	-0,04	0,17	0,64	-0,06	1					
OXY	0,41	-0,05	0,07	-0,27	0,31	0,51	-0,10	-0,10	0,46	0,08	1				
SALIN	-0,44	-0,24	-0,40	-0,22	-0,36	-0,45	-0,10	0,34	-0,55	0,06	-0,39	1			
TEMP	-0,42	0,07	-0,14	-0,09	-0,51	-0,54	0,06	0,30	-0,58	0,00	-0,84	0,50	1		
WIND	-0,04	-0,09	0,35	-0,16	-0,02	0,08	0,00	-0,15	-0,02	-0,22	0,02	-0,32	-0,09	1	
SECCHI	0,07	0,09	-0,63	0,05	-0,05	-0,13	0,00	-0,05	-0,04	-0,14	-0,09	0,26	0,20	-0,59	1

P<0.01, R ≥ 0.4737, df=26
P<0.05, R ≥ 0.3733, df=26

T24 8m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,11	1													
PP	0,00	-0,09	1												
N-NH4	0,48	0,1	-0,15	1											
N-NO2	0,33	-0,11	-0,12	0,13	1										
N-NO3	0,16	0,09	-0,11	0,00	0,55	1									
DON	-0,04	0,13	0,29	0,07	-0,32	-0,22	1								
PN	-0,06	-0,15	0,46	-0,05	-0,28	-0,26	0,42	1							
SiO2	0,35	0,08	0,07	0,24	0,57	0,53	0,07	0,02	1						
CHLa	0,12	-0,06	0,28	-0,20	0,03	0,09	0,20	0,30	0,23	1					
OXY	-0,04	0,07	-0,26	-0,34	-0,10	0,03	-0,22	-0,44	-0,24	-0,21	1				
SALIN	0,14	-0,50	0,07	0,07	0,20	-0,11	-0,09	-0,14	0,02	-0,04	0,36	1			
TEMP	-0,14	0,02	0,28	0,08	-0,32	-0,30	0,20	0,49	-0,19	0,09	-0,80	-0,49	1		
WIND	-0,10	-0,17	-0,08	-0,06	-0,16	0,07	0,09	-0,01	-0,09	-0,27	-0,05	-0,10	-0,01	1	
SECCHI	-0,04	0,16	0,05	0,01	0,06	-0,39	0,09	0,03	-0,23	0,02	0,02	0,18	0,11	-0,62	1

P<0.01, R ≥ 0.4659, df=27
P<0.05, R ≥ 0.3668, df=27

Table 13

Interestingly, negative correlation coefficients between salinity and $P\text{-}PO_4$, PP, $N\text{-}NO_3$ and SiO_2

were evidenced at station T24 surface. DOP did not correlated with salinity at surface, but was negatively correlated at the bottom. Secchi disc depth resulted to be negatively correlated with wind speed on this shallow sampling station.

T25:

T25 1m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,67	1													
PP	0,03	0,01	1												
N-NH4	0,38	0,52	0,22	1											
N-NO2	0,57	0,18	-0,21	0,08	1										
N-NO3	0,68	0,64	0,03	0,10	0,44	1									
DON	-0,41	-0,27	0,27	-0,04	-0,35	-0,27	1								
PN	-0,34	-0,44	0,16	-0,30	-0,28	-0,05	0,13	1							
SiO2	0,72	0,50	0,10	0,34	0,62	0,74	-0,12	-0,22	1						
CHLa	-0,03	-0,09	-0,20	-0,36	0,16	0,21	-0,19	0,45	-0,1	1					
OXY	0,21	0,08	0,02	-0,22	0,12	0,31	-0,15	-0,13	0,25	0,29	1				
SALIN	-0,34	-0,59	-0,32	-0,30	0,08	-0,58	0,04	-0,04	-0,38	-0,11	-0,24	1			
TEMP	-0,42	-0,18	0,13	0,01	-0,42	-0,35	0,22	0,40	-0,51	-0,14	-0,86	0,11	1		
WIND	0,03	-0,04	0,20	-0,08	-0,08	0,02	-0,04	-0,21	0,07	-0,17	0,01	-0,16	-0,08	1	
SECCHI	-0,07	-0,08	-0,41	0,06	0,13	-0,06	0,21	0,12	0,03	-0,17	-0,44	0,47	0,30	-0,43	1

P<0.01, R ≥ 0.4737, df=25
P<0.05, R ≥ 0.3733, df=25

T25 11m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,19	1													
PP	-0,07	0,31	1												
N-NH4	0,26	0,12	0,35	1											
N-NO2	0,52	0,00	-0,31	-0,10	1										
N-NO3	0,50	0,06	0,00	0,11	0,70	1									
DON	-0,46	-0,10	0,26	-0,11	-0,39	-0,50	1								
PN	-0,41	-0,30	0,27	-0,10	-0,35	-0,34	0,54	1							
SiO2	0,69	0,20	0,01	0,33	0,64	0,61	-0,47	-0,30	1						
CHLa	-0,20	-0,07	0,36	0,01	0,02	0,11	0,43	0,20	-0,05	1					
OXY	-0,09	0,13	-0,36	-0,44	0,08	0,05	-0,16	-0,39	-0,21	-0,11	1				
SALIN	-0,26	-0,03	-0,39	-0,34	0,25	0,01	-0,06	-0,16	-0,08	-0,12	0,64	1			
TEMP	-0,12	-0,15	0,47	0,13	-0,37	-0,30	0,27	0,59	-0,10	0,08	-0,85	-0,63	1		
WIND	-0,03	-0,04	0,05	-0,18	-0,15	0,03	0,12	-0,07	-0,09	-0,11	0,09	0,07	-0,10	1	
SECCHI	0,11	-0,23	-0,25	-0,10	0,08	-0,23	0,04	0,31	-0,09	-0,29	-0,20	-0,12	0,33	-0,44	1

P<0.01, R ≥ 0.4737, df=25
P<0.05, R ≥ 0.3733, df=25

Table 14

At station T25 (Tab. 14), salinity correlated negatively with DOP, N-NO_3 and SiO_2 at surface, and negatively with PP at the bottom (11m). Secchi disc depth and wind intensity resulted also negatively correlated at this station.

T03:

T03 1m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,04	1													
PP	0,37	-0,03	1												
N-NH4	0,42	0,28	0,29	1											
N-NO2	0,20	-0,11	-0,18	-0,02	1										
N-NO3	0,30	0,01	0,08	-0,14	0,32	1									
DON	-0,08	-0,17	0,12	0,26	-0,16	-0,29	1								
PN	-0,09	-0,02	0,15	-0,11	-0,20	0,06	0,10	1							
SiO2	0,69	0,05	0,34	0,22	0,36	0,78	-0,25	-0,08	1						
CHLa	0,01	0,00	0,30	-0,15	0,16	0,31	0,07	0,40	0,19	1					
OXY	0,09	0,05	0,03	-0,12	0,31	0,58	-0,14	-0,06	0,54	0,24	1				
SALIN	0,00	-0,31	-0,35	0,07	0,09	-0,44	0,10	-0,20	-0,41	-0,19	-0,48	1			
TEMP	-0,30	0,02	-0,04	0,00	-0,55	-0,62	0,22	0,24	-0,70	-0,17	-0,87	0,25	1		
WIND	-0,08	-0,25	-0,03	-0,27	-0,10	0,22	-0,23	-0,12	0,12	-0,25	-0,06	-0,23	-0,02	1	
SECCHI	-0,03	0,07	-0,35	0,15	-0,04	-0,31	0,39	-0,06	-0,32	-0,39	-0,30	0,32	0,32	-0,39	1

P<0.01, R ≥ 0.4585, df=28
P<0.05, R ≥ 0.3605, df=28

T03 14m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,62	1													
PP	-0,31	-0,17	1												
N-NH4	0,06	0,26	-0,01	1											
N-NO2	0,50	-0,02	-0,33	-0,1	1										
N-NO3	0,52	0,04	-0,26	0,19	0,68	1									
DON	-0,20	-0,13	0,56	0,09	-0,14	-0,23	1								
PN	0,14	0,24	-0,19	-0,05	-0,03	-0,12	-0,14	1							
SiO2	0,23	0,01	-0,38	0,13	0,57	0,41	-0,35	-0,04	1						
CHLa	-0,14	0,01	0,06	0,14	-0,07	0,01	0,31	-0,12	-0,18	1					
OXY	0,26	-0,07	-0,12	-0,38	0,09	0,11	0,05	-0,04	-0,17	0,04	1				
SALIN	0,20	-0,02	-0,22	-0,40	0,27	0,16	-0,04	-0,18	0,20	-0,20	0,65	1			
TEMP	-0,45	-0,03	0,41	0,30	-0,36	-0,36	0,13	0,16	-0,11	0,04	-0,87	-0,69	1		
WIND	-0,17	-0,30	0,15	-0,09	-0,15	0,05	0,19	-0,34	-0,08	-0,16	0,01	0,03	-0,07	1	
SECCHI	-0,16	0,08	0,01	-0,19	-0,08	-0,26	-0,07	0,29	-0,13	-0,24	-0,22	-0,03	0,36	-0,37	1

P<0.01, R ≥ 0.4585, df=28
P<0.05, R ≥ 0.3605, df=28

Table 15

At station T03 (Tab. 15), salinity correlated negatively with N-NO_3 and SiO_2 at surface, and negatively with N-NH_4 at the bottom (14m). Secchi disc depth and wind intensity resulted also to be negatively correlated at this station.

T08:

T08 1m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	-0,34	1													
PP	-0,09	-0,08	1												
N-NH4	-0,05	-0,13	0,19	1											
N-NO2	0,50	-0,12	0,14	0,02	1										
N-NO3	0,22	0,21	0,24	-0,08	0,31	1									
DON	-0,19	0,15	-0,04	-0,18	-0,28	0,39	1								
PN	-0,20	-0,18	0,33	0,57	-0,18	-0,27	-0,01	1							
SiO2	0,27	0,05	0,41	0,02	0,49	0,74	0,20	0,04	1						
CHLa	0,36	-0,20	0,34	0,07	0,16	0,37	0,25	0,03	0,36	1					
OXY	0,40	0,02	0,00	-0,19	0,32	0,56	0,18	-0,38	0,50	0,25	1				
SALIN	0,03	0,03	-0,46	-0,17	0,20	-0,43	-0,31	-0,05	-0,20	-0,42	-0,08	1			
TEMP	-0,47	-0,03	-0,01	0,08	-0,50	-0,55	-0,12	0,35	-0,59	-0,29	-0,89	-0,1	1		
WIND	-0,05	-0,30	-0,20	-0,23	-0,12	-0,26	-0,11	-0,38	-0,24	-0,29	-0,12	0,29	-0,02	1	
SECCHI	-0,21	0,30	-0,31	0,07	-0,19	-0,23	0,05	0,09	-0,34	-0,46	-0,36	-0,02	0,44	-0,31	1

P<0.01, R ≥ 0.4659, df=27
P<0.05, R ≥ 0.3668, df=27

T08 23m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	-0,16	1													
PP	0,13	-0,04	1												
N-NH4	0,42	0,01	0,36	1											
N-NO2	0,39	-0,15	-0,30	-0,25	1										
N-NO3	0,30	-0,14	-0,20	-0,02	0,63	1									
DON	-0,22	-0,18	-0,16	-0,14	-0,15	-0,21	1								
PN	0,29	-0,20	0,29	0,01	0,06	-0,21	0,07	1							
SiO2	0,53	-0,25	0,27	0,47	0,12	0,15	-0,14	0,15	1						
CHLa	0,26	0,04	0,45	-0,08	-0,11	-0,16	0,00	0,54	0,10	1					
OXY	-0,53	0,16	-0,65	-0,73	0,11	-0,02	0,25	-0,19	-0,53	-0,10	1				
SALIN	-0,23	0,06	-0,25	-0,36	0,13	0,02	0,19	-0,17	0,00	-0,09	0,47	1			
TEMP	0,44	-0,22	0,71	0,48	-0,17	-0,05	-0,18	0,33	0,40	0,29	-0,85	-0,60	1		
WIND	-0,31	-0,23	0,11	-0,09	-0,20	0,00	0,42	-0,24	-0,21	-0,23	-0,05	0,17	-0,02	1	
SECCHI	0,43	0,22	0,36	0,31	-0,10	-0,28	-0,01	0,35	0,35	0,31	-0,29	0,06	0,33	-0,31	1

P<0.01, R ≥ 0.4659, df=27
P<0.05, R ≥ 0.3668, df=27

Table 16

At T08 (Tab. 16), a station located in the central part of the Gulf, salinity correlated negatively with PP and nitrates at the surface, but not with any form of nutrient at the bottom (23m). No correlation between Secchi depth and wind intensity could be evidenced. A significant negative correlation between Secchi disc depth and Chlorophyll *a* was found at the surface.

T26:

T26 1m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	-0,01	1													
PP	0,42	0,07	1												
N-NH4	0,44	0,15	0,51	1											
N-NO2	0,34	0,09	0,01	-0,18	1										
N-NO3	0,30	0,49	0,42	0,20	0,44	1									
DON	0,05	-0,21	0,10	0,03	-0,17	-0,11	1								
PN	-0,10	-0,24	0,23	-0,04	-0,23	-0,21	0,07	1							
SiO2	0,23	0,31	0,35	0,29	0,52	0,68	-0,05	-0,16	1						
CHLa	0,02	0,08	0,53	0,22	0,19	0,28	-0,13	-0,25	0,18	1					
OXY	0,03	0,04	0,12	-0,27	0,30	0,45	-0,14	-0,33	0,35	0,33	1				
SALIN	-0,17	-0,30	-0,58	-0,13	0,24	-0,40	0,00	-0,20	-0,22	-0,07	0,02	1			
TEMP	-0,10	-0,13	-0,09	0,04	-0,45	-0,45	0,14	0,51	-0,47	-0,39	-0,88	-0,27	1		
WIND	-0,23	0,13	-0,34	-0,13	-0,18	-0,31	-0,16	-0,12	-0,18	-0,40	-0,14	0,30	-0,04	1	
SECCHI	-0,18	-0,20	-0,49	-0,19	-0,27	-0,39	0,07	0,06	-0,38	-0,43	-0,41	0,11	0,48	-0,21	1

P<0.01, R ≥ 0.4659, df=27
P<0.05, R ≥ 0.3668, df=27

T26 23m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,00	1													
PP	0,19	-0,09	1												
N-NH4	0,82	0,14	0,22	1											
N-NO2	0,13	-0,02	-0,18	-0,14	1										
N-NO3	0,29	0,20	-0,04	0,15	0,53	1									
DON	0,18	-0,32	0,06	0,21	-0,13	-0,22	1								
PN	-0,17	-0,23	0,00	0,07	0,05	-0,18	0,2	1							
SiO2	0,72	-0,06	0,20	0,70	0,07	0,35	0,16	0,02	1						
CHLa	-0,12	-0,05	0,68	-0,08	-0,15	-0,01	-0,03	-0,10	-0,12	1					
OXY	-0,70	0,10	-0,38	-0,79	0,11	-0,14	-0,25	0,00	-0,62	-0,04	1				
SALIN	-0,05	0,15	-0,12	-0,26	0,17	0,02	-0,44	-0,08	-0,01	-0,15	0,48	1			
TEMP	0,41	-0,27	0,49	0,51	-0,18	0,09	0,43	0,08	0,47	0,17	-0,87	-0,60	1		
WIND	0,08	-0,15	0,03	0,02	-0,18	0,02	0,16	-0,19	-0,01	0,01	-0,12	-0,04	0,11	1	
SECCHI	0,06	-0,14	0,18	0,08	-0,23	-0,37	-0,06	0,32	0,11	-0,13	-0,20	0,16	0,25	-0,19	1

P<0.01, R ≥ 0.4737, df=26
P<0.05, R ≥ 0.3733, df=26

Table 17

As observed at station T08, salinity correlated negatively with PP and nitrates at the surface, while, at the bottom (23m), a negative correlation with DON was found. No correlation between Secchi depth

and wind intensity could be evidenced, but also on T26 (Tab. 17) a significant negative correlation between Secchi disc depth and Chlorophyll *a* was found at 1m.

T11:

T11 1m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	-0,17	1													
PP	-0,06	0,04	1												
N-NH4	-0,04	-0,04	0,14	1											
N-NO2	0,42	-0,01	-0,18	-0,26	1										
N-NO3	0,49	0,29	0,06	-0,21	0,38	1									
DON	-0,33	-0,16	0,19	0,04	-0,25	-0,38	1								
PN	0,00	-0,10	0,20	-0,33	-0,11	-0,18	0,36	1							
SiO2	0,32	-0,01	0,34	-0,21	0,48	0,59	-0,17	0,04	1						
CHLa	0,09	-0,03	-0,22	0,11	0,34	0,27	-0,12	-0,08	0,36	1					
OXY	0,28	0,12	-0,24	-0,35	0,28	0,47	-0,29	0,13	0,44	0,22	1				
SALIN	-0,07	0,04	-0,20	0,13	0,20	-0,37	0,09	0,00	-0,13	-0,09	0,01	1			
TEMP	-0,24	-0,05	0,21	0,14	-0,42	-0,47	0,30	0,08	-0,50	-0,37	-0,86	-0,23	1		
WIND	-0,20	-0,31	-0,05	0,02	-0,14	-0,32	0,07	-0,22	-0,20	-0,32	-0,08	0,31	-0,05	1	
SECCHI	-0,35	0,25	-0,09	0,03	-0,33	-0,37	0,50	0,15	-0,60	-0,55	-0,43	0,11	0,49	0,02	1

P<0.01, R ≥ 0.4737, df=26
P<0.05, R ≥ 0.3733, df=26

T11 23m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	-0,06	1													
PP	0,02	-0,05	1												
N-NH4	0,66	0,02	0,22	1											
N-NO2	0,24	-0,02	-0,40	-0,19	1										
N-NO3	0,27	-0,18	-0,21	0,02	0,55	1									
DON	0,07	-0,20	-0,01	0,02	-0,11	-0,26	1								
PN	0,07	-0,25	0,48	0,15	-0,36	-0,18	0,20	1							
SiO2	0,82	-0,16	0,10	0,64	0,16	0,29	0,11	0,37	1						
CHLa	-0,14	-0,04	0,50	-0,04	-0,10	-0,14	0,02	0,10	-0,19	1					
OXY	-0,49	-0,15	-0,29	-0,72	0,16	0,04	0,05	-0,13	-0,57	0,04	1				
SALIN	-0,05	-0,10	-0,01	-0,32	0,09	0,14	0,03	0,07	-0,02	-0,13	0,39	1			
TEMP	0,23	0,04	0,43	0,51	-0,23	-0,09	0,09	0,27	0,36	0,23	-0,83	-0,56	1		
WIND	0,01	-0,28	0,11	0,04	-0,19	0,04	0,00	-0,13	-0,02	-0,05	-0,04	0,30	-0,10	1	
SECCHI	-0,11	0,26	0,20	0,07	-0,18	-0,31	-0,13	0,34	-0,05	-0,10	-0,19	0,03	0,29	-0,04	1

P<0.01, R ≥ 0.4659, df=27
P<0.05, R ≥ 0.3668, df=27

Table 18

At station T11 (Tab. 18), the southernmost sampling station, no correlation between salinity and any forms of nutrients could be evidenced. A significant negative correlation between Secchi disc depth and Chlorophyll *a* was found at the surface while at the bottom (23m) a positive correlation was evidenced between PP and Chlorophyll *a*.

C1:

C1 1m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,01	1													
PP	0,02	0,17	1												
N-NH4	0,27	-0,07	0,14	1											
N-NO2	0,32	-0,03	0,03	0,14	1										
N-NO3	0,31	0,07	0,39	-0,02	0,15	1									
DON	-0,04	0,16	-0,10	0,00	-0,03	-0,22	1								
PN	-0,24	-0,06	0,23	0,00	-0,28	0,03	0,10	1							
SiO2	0,49	-0,05	0,46	0,08	0,29	0,73	-0,22	0,12	1						
CHLa	-0,01	0,00	0,25	-0,03	0,24	0,37	0,11	0,09	0,23	1					
OXY	0,24	0,06	-0,20	-0,02	0,33	0,31	-0,05	-0,21	0,18	0,48	1				
SALIN	-0,16	-0,12	-0,56	-0,02	0,21	-0,70	0,16	-0,25	-0,59	-0,24	0,09	1			
TEMP	-0,31	0,03	0,18	-0,01	-0,52	-0,29	0,01	0,28	-0,28	-0,45	-0,84	-0,25	1		
WIND	0,10	-0,19	-0,23	-0,03	0,02	-0,15	-0,16	-0,15	-0,10	-0,08	0,10	0,20	-0,17	1	
SECCHI	-0,08	-0,12	-0,55	-0,12	-0,06	-0,26	-0,03	-0,26	-0,28	-0,44	-0,09	0,34	0,13	0,02	1

P<0.01, R ≥ 0.3005, df=68
P<0.05, R ≥ 0.2351, df=68

C1 15m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	-0,03	1													
PP	-0,06	-0,05	1												
N-NH4	0,05	-0,13	0,11	1											
N-NO2	0,61	-0,08	-0,16	-0,03	1										
N-NO3	0,63	-0,09	-0,20	-0,03	0,93	1									
DON	0,10	0,30	0,01	-0,16	-0,05	-0,06	1								
PN	-0,29	-0,12	0,22	0,15	-0,21	-0,28	-0,03	1							
SiO2	0,67	-0,07	0,07	0,27	0,62	0,64	-0,01	0,03	1						
CHLa	-0,33	-0,10	0,21	-0,14	-0,11	-0,20	-0,13	0,24	-0,33	1					
OXY	-0,24	-0,03	-0,27	-0,51	-0,15	-0,12	-0,15	-0,25	-0,48	0,16	1				
SALIN	-0,06	0,06	-0,15	-0,32	-0,17	-0,14	-0,08	-0,36	-0,26	-0,04	0,52	1			
TEMP	-0,01	0,03	0,34	0,32	-0,11	-0,17	0,20	0,46	0,19	-0,01	-0,83	-0,67	1		
WIND	-0,01	-0,22	0,14	0,36	-0,05	0,05	-0,13	0,03	-0,01	-0,15	0,02	0,17	-0,20	1	
SECCHI	0,14	-0,06	0,05	-0,06	-0,05	-0,07	-0,07	0,08	-0,09	-0,16	-0,13	0,18	0,16	0,06	1

P<0.01, R ≥ 0.3111, df=65
P<0.05, R ≥ 0.2404, df=65

Table 19

The coastal C1 is the easternmost sampling station. Here (Tab. 19) salinity correlated negatively with PP, nitrates, PN, SiO_2 and Chlorophyll *a* at the surface while, at the bottom (15m), a negative correlation could be found with N-NH_4, PN and SiO_2. A positive correlation was evidenced between PP and Chlorophyll *a* at the surface. Wind intensity correlated positively with ammonium concentration at the bottom, but did not correlate with Secchi disc depth.

T22:

T22 1m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,21	1													
PP	0,11	0,39	1												
N-NH4	0,04	-0,16	0,02	1											
N-NO2	0,51	-0,03	-0,24	0,10	1										
N-NO3	0,40	0,11	0,45	0,18	0,30	1									
DON	-0,15	-0,16	-0,31	-0,19	-0,24	-0,09	1								
PN	-0,06	0,23	0,67	-0,10	-0,36	0,13	-0,15	1							
SiO2	0,34	-0,08	0,30	0,28	0,29	0,84	-0,02	-0,07	1						
CHLa	0,33	0,17	0,40	-0,13	0,42	0,65	-0,26	0,21	0,35	1					
OXY	0,39	-0,08	-0,03	0,04	0,55	0,47	-0,29	-0,16	0,38	0,44	1				
SALIN	-0,15	-0,34	-0,59	0,03	0,14	-0,72	-0,07	-0,41	-0,58	-0,47	-0,01	1			
TEMP	-0,47	-0,01	0,16	-0,15	-0,66	-0,35	0,34	0,37	-0,27	-0,33	-0,89	-0,21	1		
WIND	0,10	0,00	0,08	0,28	-0,11	-0,15	-0,03	0,13	-0,08	-0,11	0,11	0,13	-0,14	1	
SECCHI	-0,34	-0,29	-0,58	-0,09	-0,22	-0,39	0,27	-0,27	-0,36	-0,54	-0,39	0,33	0,30	-0,11	1

P<0.01, R ≥ 0.4905, df=24
P<0.05, R ≥ 0.3876, df=24

T22 18m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	0,16	1													
PP	-0,06	-0,24	1												
N-NH4	0,45	0,03	0,29	1											
N-NO2	0,28	0,24	-0,31	-0,09	1										
N-NO3	0,43	0,01	-0,33	-0,02	0,61	1									
DON	0,12	-0,25	0,43	0,17	-0,19	0,01	1								
PN	-0,02	-0,28	0,47	0,28	-0,09	-0,16	0,04	1							
SiO2	0,31	-0,13	0,16	0,52	-0,09	0,11	-0,24	0,52	1						
CHLa	-0,21	0,12	0,36	-0,17	0,01	-0,07	0,25	0,40	-0,1	1					
OXY	-0,15	0,18	-0,55	-0,53	0,12	0,12	-0,17	-0,48	-0,58	-0,11	1				
SALIN	0,02	0,12	-0,26	-0,33	-0,12	-0,16	-0,27	-0,28	-0,08	-0,10	0,38	1			
TEMP	0,02	-0,25	0,71	0,41	-0,26	-0,24	0,30	0,47	0,39	0,18	-0,89	-0,59	1		
WIND	0,15	0,12	-0,03	0,25	-0,06	-0,03	0,08	-0,11	0,02	-0,15	0,08	0,19	-0,18	1	
SECCHI	0,09	-0,25	0,15	0,13	0,00	-0,20	0,10	0,24	0,07	0,01	-0,39	0,00	0,35	-0,11	1

P<0.01, R ≥ 0.4737, df=26
P<0.05, R ≥ 0.3733, df=26

Table 20

As observed at station C1 salinity correlated negatively with PP (Tab. 20), nitrates, PN, SiO_2 and Chlorophyll *a* at the surface where a positive correlation between PP and Chlorophyll *a* could be noted. Negative correlations between Secchi disc depth and PP, nitrates and Chlorophyll *a* were found at the surface. Wind intensity did not correlate with Secchi disc depth.

T23:

T23 1m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	-0,12	1													
PP	0,35	0,21	1												
N-NH4	-0,20	0,10	0,01	1											
N-NO2	0,01	0,11	-0,26	0,03	1										
N-NO3	0,16	0,32	0,57	-0,16	0,01	1									
DON	-0,23	-0,29	0,02	0,07	-0,40	-0,20	1								
PN	0,33	0,02	0,60	0,35	-0,20	0,15	0,05	1							
SiO2	0,23	0,15	0,57	0,01	0,00	0,72	0,10	0,26	1						
CHLa	0,06	0,15	0,27	-0,05	0,28	0,40	0,01	0,28	0,24	1					
OXY	0,05	-0,07	-0,06	-0,28	0,49	0,35	-0,20	-0,25	0,29	0,30	1				
SALIN	0,05	-0,49	-0,59	0,04	0,32	-0,81	0,13	-0,25	-0,48	-0,29	0,03	1			
TEMP	-0,13	0,05	0,19	0,17	-0,66	-0,18	0,13	0,23	-0,32	-0,29	-0,88	-0,27	1		
WIND	0,17	0,00	0,20	-0,05	-0,12	-0,01	0,22	0,01	0,09	-0,17	0,11	0,07	-0,11	1	
SECCHI	-0,17	-0,21	-0,31	0,24	-0,06	-0,34	-0,11	0,11	-0,39	-0,43	-0,28	0,27	0,30	-0,14	1

P<0.01, R ≥ 0.4659, df=27
P<0.05, R ≥ 0.3668, df=27

T23 18m.

	P-PO4	DOP	PP	N-NH4	N-NO2	N-NO3	DON	PN	SiO2	CHLa	OXY	SALIN	TEMP	WIND	SECCHI
P-PO4	1														
DOP	-0,34	1													
PP	-0,23	-0,05	1												
N-NH4	0,00	-0,10	0,22	1											
N-NO2	-0,03	0,01	-0,29	-0,11	1										
N-NO3	0,29	-0,06	-0,34	0,14	0,71	1									
DON	-0,03	-0,30	0,30	-0,02	-0,03	0	1								
PN	-0,04	-0,24	0,28	0,30	-0,03	-0,05	0,04	1							
SiO2	0,02	-0,20	0,09	0,44	0,11	0,18	0,07	0,64	1						
CHLa	-0,15	0,00	0,37	-0,11	0,23	-0,10	0,47	0,51	0,24	1					
OXY	0,26	0,01	-0,51	-0,65	0,06	0,08	-0,11	-0,48	-0,56	-0,30	1				
SALIN	0,12	0,05	-0,12	-0,54	0,00	-0,05	-0,02	-0,06	0,00	0,02	0,49	1			
TEMP	-0,32	-0,08	0,62	0,50	-0,27	-0,33	0,08	0,34	0,32	0,20	-0,87	-0,62	1		
WIND	0,20	-0,04	-0,02	0,26	-0,01	0,24	0,07	-0,02	-0,11	-0,18	0,14	0,14	-0,21	1	
SECCHI	-0,15	-0,30	0,39	0,31	-0,02	-0,02	0,32	0,42	0,31	0,31	-0,46	-0,17	0,39	-0,14	1

P<0.01, R ≥ 0.4905, df=24
P<0.05, R ≥ 0.3876, df=24

Table 21

At the station T23 (Tab. 21), salinity correlated negatively with DOP, PP, nitrate and SiO_2 at the surface while, at the bottom, a negative correlation could be found with N-NH_4. Wind intensity but did not correlate with Secchi disc depth, but negative correlations between Secchi disc depth and SiO_2 and Chlorophyll *a* was found at the surface**.**

2.4. Temporal variations of surface nutrient concentrations at three stations (A0, A2, A3) near the city of Trieste (2002-2005)

2.4.1. Introduction

To evaluate the impact of Trieste anthropic inputs on marine ecosystem, a monitoring program was carried out in the period from January 2002 to December 2005 in the framework of the Italian Environmental Ministry monitoring program. Surface seawater was fortnightly collected at three stations (A0, A2, A3) located in front of the city (Fig.1).

A total of 252 samples were collected and analyzed for seven environmental parameters: N-NH_4, N-NO_2, N-NO_3, P-PO_4, SiO_2, Total Nitrogen (TN) and Total Phosphorus (TP) concentrations.

2.4.2. Methods

For inorganic nutrients determinations, water samples were filtered on GF/F glass fiber filters (0.7µm nominal pore size, 47mm diameter, Whatman International Ltd). TN and TP concentrations were determined using a persulfate digestion procedure (Grasshoff et al. 1983). After the step of oxidation, total dissolved nitrogen and phosphorus were determined with the same automated colorimetric methods used for nitrate and reactive phosphorus. Inorganic nutrients and TN and TP analyses were until March 2003 conducted at room temperature on a five-channel Alliance Integral Continuous Flow Analyser, using standard procedures. From April 2003 to December 2005 analyses were conducted on a Bran+Luebbe Autoanalyser3 Continuous Flow Analyser (Bran+Luebbe, Norderstedt, Germany) using standard procedures (Bran+Luebbe 2003a,b,c,d,e and references

therein). The efficiency of the system was checked before and after sample analyses by replicating calibration standards.

At each sampling station, a CTD profile was recorded using a Seabird19 Plus multiparametric probe, which was calibrated every 6 months. Salinity was computed, according to the UNESCO formula for salinity determination (UNESCO 1978), from measurements of hydrostatic pressure, temperature and conductivity.

2.4.3. Results

2.4.3.1 Main hydrological features

Descriptive statistics of the main hydrological features of each station are summarized in Table 22.

A0

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Secchi depth [m]	Chl *a* [µg/L]
Max	38.47	28.15	7.46	17.1	2.43
Min	31.28	6.47	3.93	3.5	0.02
Median	37.66	15.27	5.44	8.7	0.70
Average	37.30	15.83	5.49	9.0	0.77
Std.Dev.	1.19	6.50	0.74	2.8	0.49

A2

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Secchi depth [m]	Chl *a* [µg/L]
Max	38.43	27.71	7.53	17.5	2.80
Min	28.89	6.44	3.91	2.9	0.00
Median	37.68	15.23	5.39	8.4	0.69
Average	37.18	15.89	5.50	8.8	0.69
Std.Dev.	1.53	6.46	0.73	2.9	0.46

A3

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Secchi depth [m]	Chl *a* [µg/L]
Max	38.41	28.01	7.62	15.6	6.67
Min	28.93	6.40	4.10	3.0	0.00
Median	37.65	15.31	5.49	9.4	0.69
Average	37.23	15.94	5.52	9.1	0.76
Std.Dev.	1.44	6.45	0.73	2.7	0.81

Table 22.

A very high chlorophyll *a* value was registered in November 2003 at station A3, but the median chlorophyll *a* values on the three stations were very similar. The lowest salinity value was reached at all stations in May 2005, while the lowest water temperature was recorded at station A3 in March 2005. Median Secchi disc depths at the three stations were similar to the ones registered at stations

T11 (9.5m.) and T23 (9m.), even if the period of monitoring was different.

2.4.3.2. Spatial distribution and temporal variation of nutrients

Descriptive statistics of dissolved inorganic nutrients and TN and TP are summarized in the following tables.

Table 23 report the descriptive statistics for the spatial distribution of inorganic nutrients and TN and TP in the period of investigation.

A0

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	$P\text{-}PO_4$ µM	SiO_2 µM	TN µM	TP µM
Max	3.02	1.33	12.55	0.35	8.99	29.35	3.53
Min	< 0.03	0.00	0.03	< 0.02	0.06	1.34	0.08
Median	0.81	0.13	0.91	0.08	1.75	10.75	0.63
Average	0.94	0.24	1.80	0.09	2.40	11.87	0.74
Std.Dev.	0.62	0.29	2.30	0.07	1.85	5.13	0.59

A2

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	$P\text{-}PO_4$ µM	SiO_2 µM	TN µM	TP µM
Max	4.74	1.31	11.93	0.38	9.42	36.86	3.16
Min	< 0.03	0.00	0.02	< 0.02	< 0.01	1.75	0.07
Median	0.84	0.10	0.94	0.07	1.82	10.25	0.60
Average	0.91	0.22	1.56	0.09	2.15	11.24	0.66
Std.Dev.	0.69	0.28	1.97	0.08	1.69	5.98	0.51

A3

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	$P\text{-}PO_4$ µM	SiO_2 µM	TN µM	TP µM
Max	2.88	1.29	19.89	0.30	10.85	46.33	5.60
Min	< 0.03	0.00	0.02	< 0.02	< 0.01	1.18	0.09
Median	0.79	0.11	0.77	0.07	1.93	10.20	0.60
Average	0.88	0.22	1.71	0.08	2.24	11.56	0.72
Std.Dev.	0.63	0.28	2.59	0.06	1.78	7.17	0.70

Table 23

The descriptive statistics of total and dissolved inorganic nutrient rations are presented in Table 24.

A0

	DIN:DIP	Si:DIP	Si:DIN
Max	2001.2	1772.4	4.50
Min	3.2	0.7	0.09
Median	40.1	28.7	0.82
Average	77.2	69.8	1.03
Std.Dev.	224.4	226.8	0.85

A2

	DIN:DIP	Si:DIP	Si:DIN
Max	1934.7	2031.3	15.06
Min	2.4	0.1	0.00
Median	31.1	26.8	0.83
Average	81.4	75.5	1.39
Std.Dev.	236.8	259.2	2.04

A3

	DIN:DIP	Si:DIP	Si:DIN
Max	1173.9	559.9	15.42
Min	2.5	0.6	0.00
Median	32.3	28.2	0.87
Average	63.7	43.1	1.39
Std.Dev.	146.5	76.7	2.03

Table 24

Median dissolved inorganic N:P ratios (DIN:DIP) resulted to be similar at station A2 and A3, and the value was slightly higher at station A0. Median Si:DIP ratio resulted to be lower compared to the values found at the other stations in the Gulf, mainly do to lower SiO_2 concentrations. Median inorganic Si:DIN ratios resulted to be similar to the other stations in the Gulf..

2.4.3.2.1. Ammonium

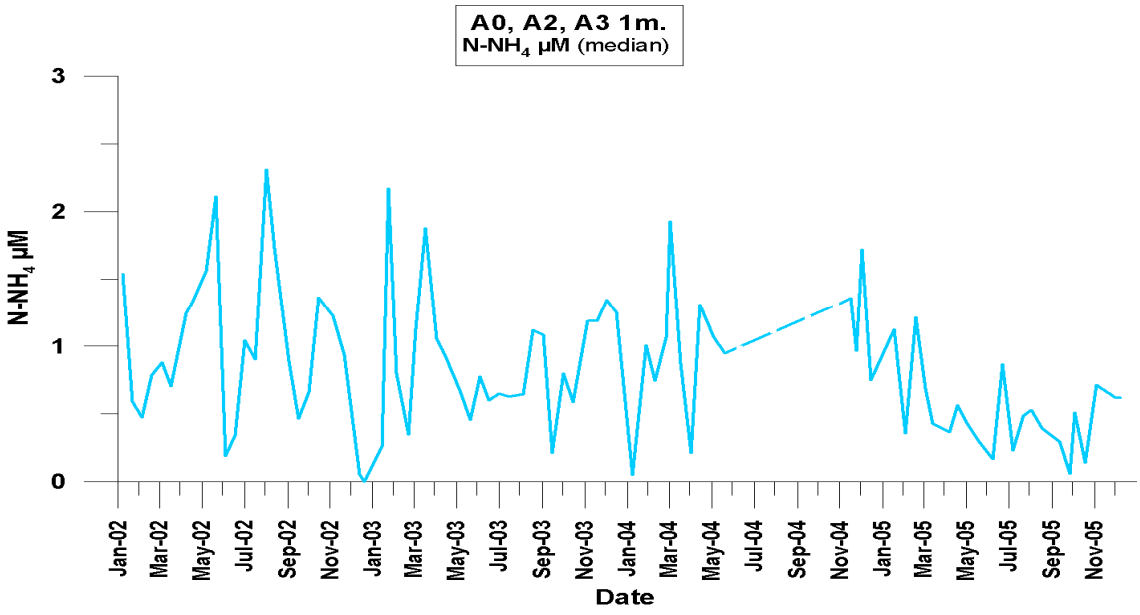

Fig. 13

Ammonium concentration on the three stations did not show a clear yearly trend. Highest value was found in January 2003 at station A3. The median ammonium concentration calculated on whole period of investigation resulted to be rather similar, around 0.8µM, at all stations.

2.4.3.2.2. Nitrite

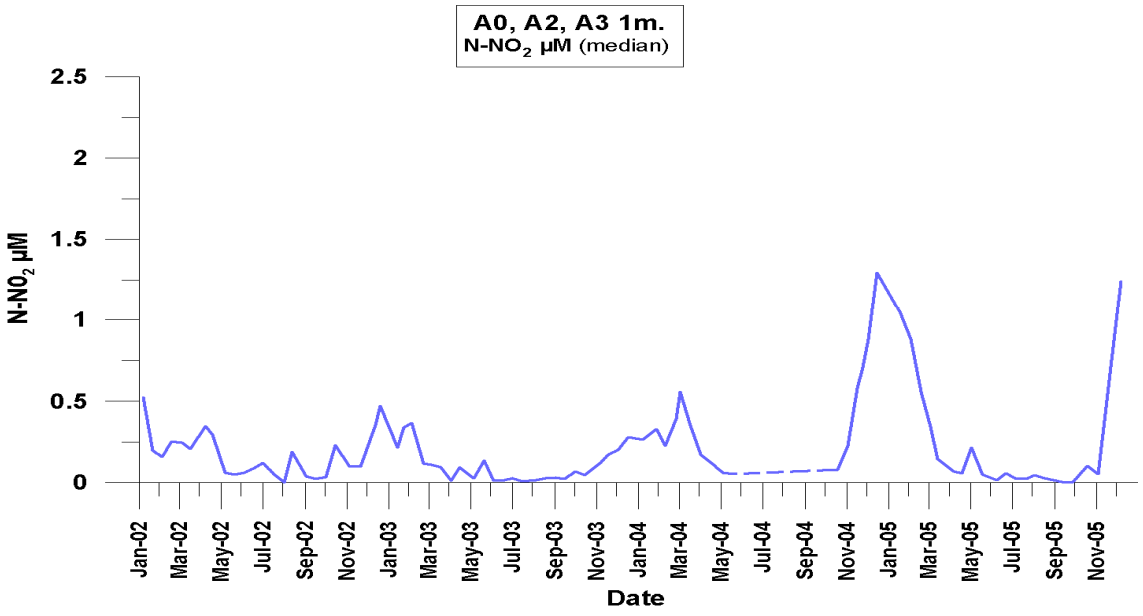

Fig. 14

As for the other sampling stations in the Gulf a clear visible yearly trend in nitrite content was notable at these stations, with highest monthly median values found in the winter months and the lowest ones in the summers. Overall highest nitrite concentration was registered in December 2005 at station A2, but as for ammonium, median nitrite values resulted very similar at all stations, around 0.12µM.

2.4.3.2.3. Nitrate

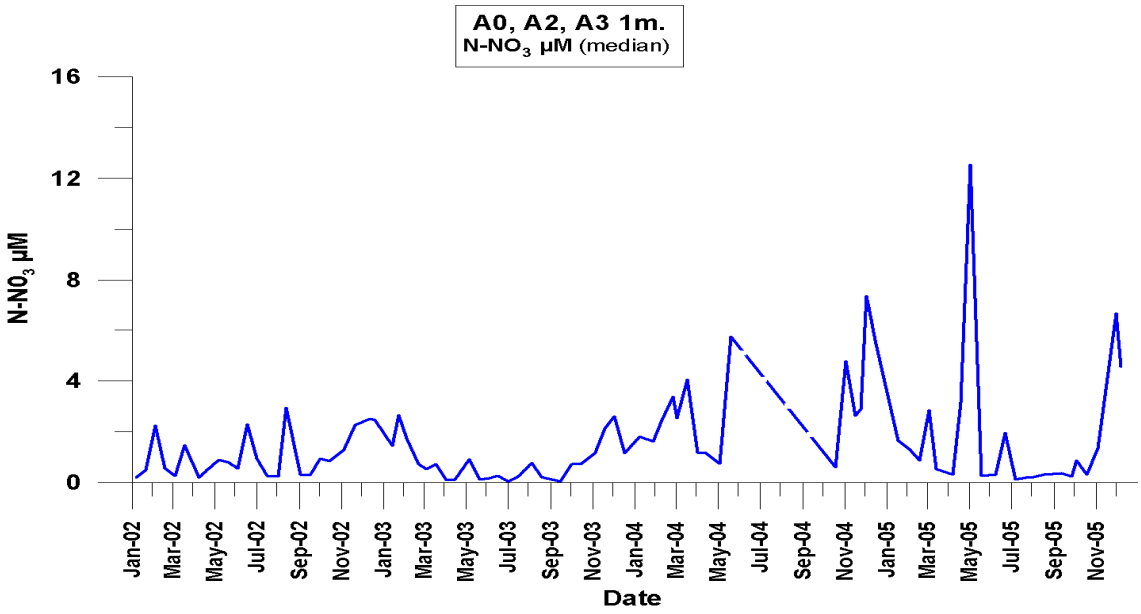

Fig. 15

The clear seasonal variation of nitrates could be noticed until May 2004, with relatively high

late autumn and winter concentrations and low summer values. Highest nitrate value was found in May 2005 at all stations, which was also the month where the lowest salinity value was recorded. The median nitrate concentration calculated on whole period of investigation resulted to be similar at A0 and A2 stations, around 0.92µM.

2.4.3.2.4 Phosphate

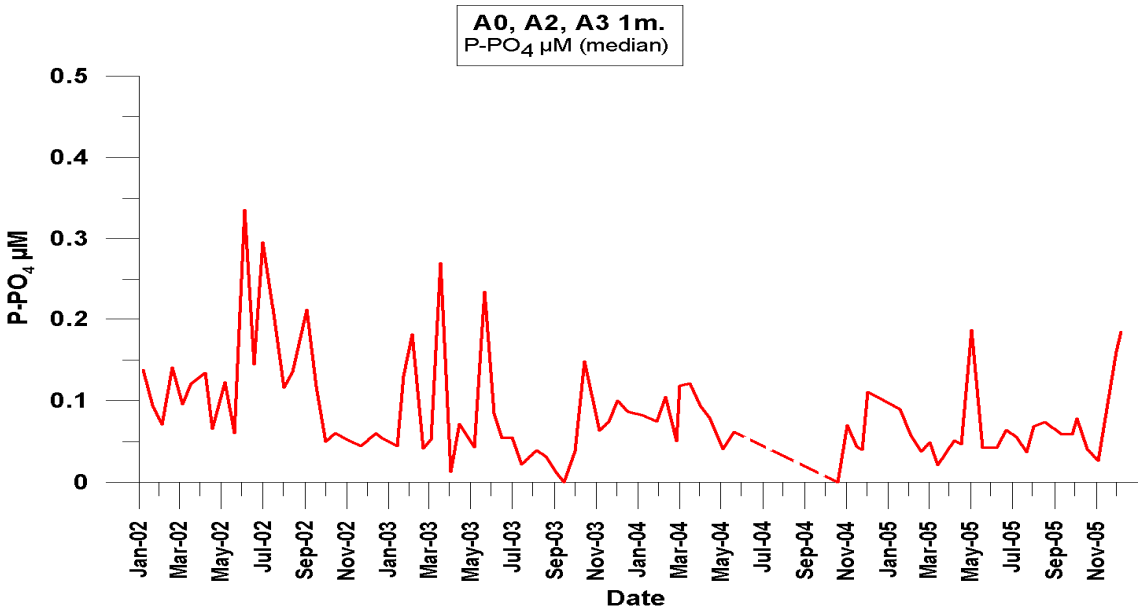

Fig. 16

Relatively high phosphate concentrations were registered in June and July 2002 at all stations. Median phosphate concentrations calculated on the three years of monitoring were nearly identical at all stations, 0.07-0.08 µM.

2.4.3.2.5. Silicate

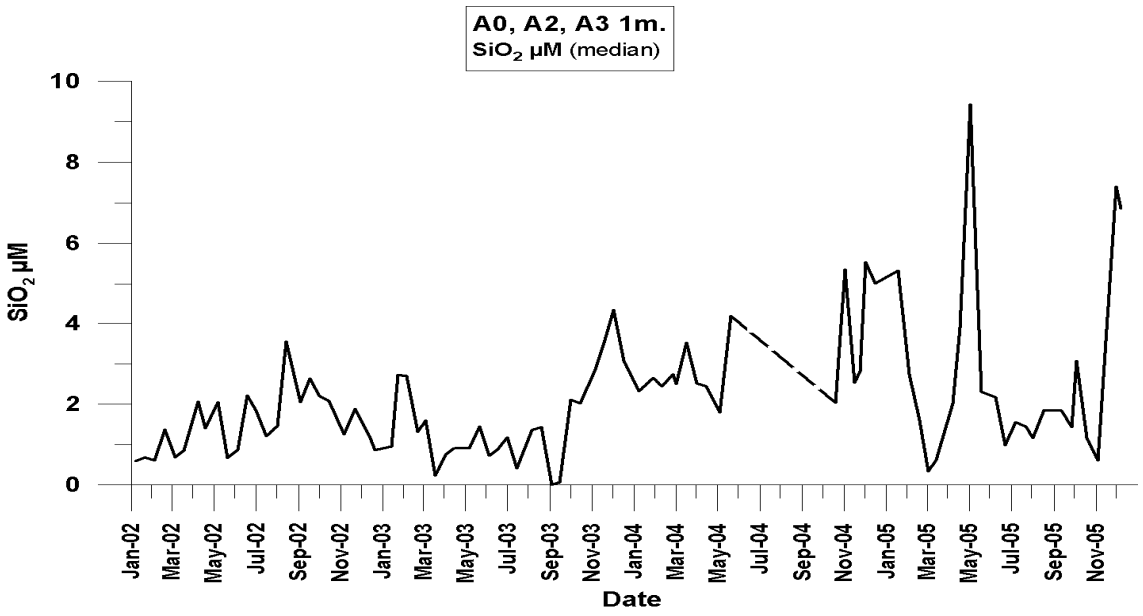

Fig. 17

The temporal evolution of silicate did not make in evidence a clear seasonal variation. Highest concentrations were, as for the nitrates recorded in May 2005. Median silicate concentrations, calculated on the three years of monitoring, resulted to be somewhat lower at these stations compared to the ones in the center of the Gulf. However, this could be do to the lower concentrations evidenced in 2002 and 2003 at stations A0, A2 and A3.

2.4.3.2.6. Total Nitrogen (TN)

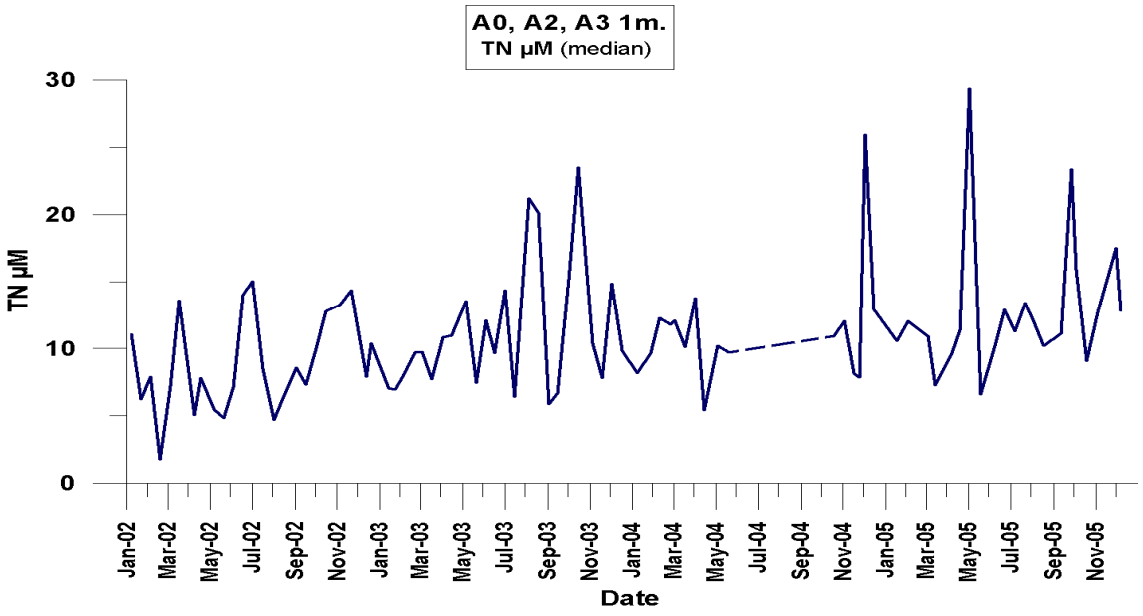

Fig. 18

Highest Total Nitrogen concentrations were as for the nitrates and silicates, recorded in May 2005. Median TN values resulted to be similar between the stations and no clear seasonal variation could be noted. However, median TN values resulted to be a little higher at the end of the monitoring period.

2.4.3.2.7. Total Phosphorus (TP)

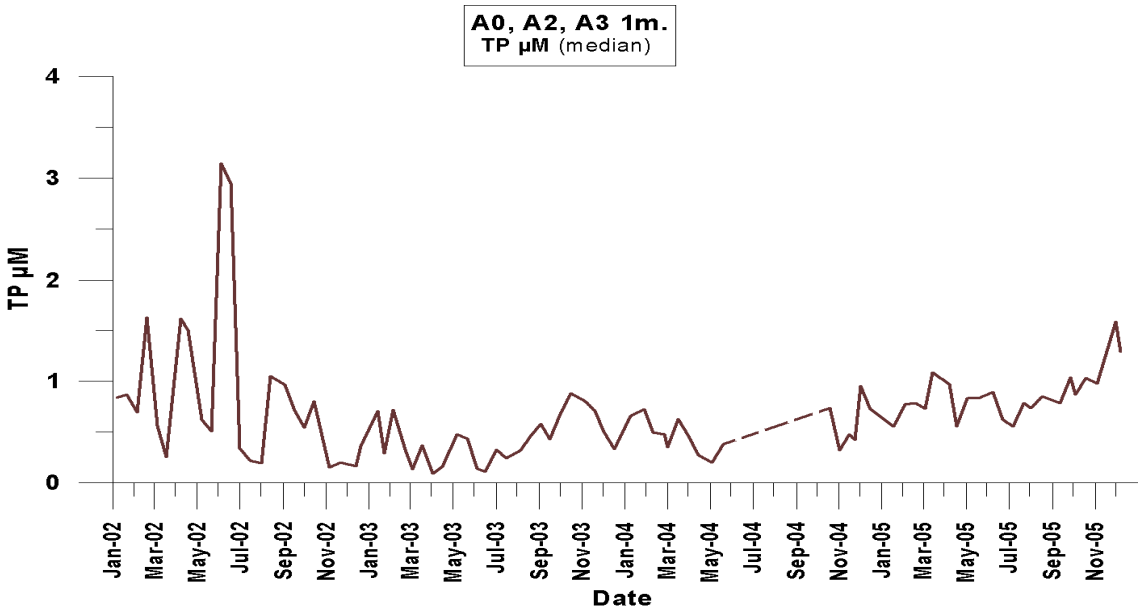

Fig. 19

Highest TP values were recorded in June 2002 at all stations, when also relative low salinity values were registered. No clear seasonal trend was notable and median TP concentration calculated on whole period of investigation resulted to be rather similar at all stations, around 0,6µM.

2.4.3.4. Principal Component Analysis

PCA was carried out according to the same methods and principles previously described in chapter 2.3.3.6.

Following variables were considered: Dissolved inorganic nutrients ($N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, $P\text{-}PO_4$, SiO_2), Total Nitrogen (TN) and Total Phosphorus (TP), Chlorophyll *a*, dissolved oxygen (OXY), salinity (SAL), temperature (TEMP), wind intensity (WIND) and Secchi disc depth (SECCHI). Wind intensity was calculated as average of wind intensity on the sampling date and on the two days preceding the sampling date. Secchi disc depth was used as an indicator of water column transparency. The PCA was performed on each sampling station independently and bi-plots are reported in Appendix. Cross-correlations tables are showed for each station.

A0 1m.

	P-PO4	TP	N-NH4	N-NO2	N-NO3	TN	SiO2	CHLa	OXY	SALIN	TEMP	SECCHI	WIND
P-PO4	1												
TP	0,22	1											
N-NH4	0,37	-0,16	1										
N-NO2	0,15	0,04	0,23	1									
N-NO3	0,22	0,00	0,21	0,45	1								
TN	0,08	0,14	-0,02	0,22	0,39	1							
SiO2	0,22	-0,01	0,21	0,39	0,70	0,30	1						
CHLa	0,14	-0,15	0,19	0,09	0,21	0,10	0,10	1					
OXY	0,01	-0,10	-0,04	0,22	0,18	-0,10	0,03	0,08	1				
SALIN	-0,28	-0,20	-0,12	0,06	-0,58	-0,32	-0,51	-0,10	0,07	1			
TEMP	0,01	0,09	-0,07	-0,44	-0,22	0,17	-0,07	-0,15	-0,84	-0,26	1		
SECCHI	-0,04	-0,16	0,06	-0,10	-0,29	-0,20	-0,20	-0,27	-0,01	0,28	0,06	1	
WIND	0,00	-0,05	0,08	-0,01	-0,19	-0,22	-0,19	-0,09	0,03	0,37	-0,13	0,04	1

P<0.01, R ≥ 0.2752, df=84
P<0.05, R ≥ 0.2120, df=84

A2 1m.

	P-PO4	TP	N-NH4	N-NO2	N-NO3	TN	SiO2	CHLa	OXY	SALIN	TEMP	SECCHI	WIND
P-PO4	1												
TP	0,26	1											
N-NH4	0,06	-0,20	1										
N-NO2	0,07	0,12	0,08	1									
N-NO3	0,10	0,07	0,10	0,51	1								
TN	-0,09	0,04	-0,17	0,10	0,32	1							
SiO2	0,18	0,13	0,06	0,56	0,80	0,38	1						
CHLa	0,07	-0,14	0,08	0,05	-0,03	-0,17	-0,03	1					
OXY	0,00	-0,07	0,09	0,29	0,11	-0,15	-0,05	0,19	1				
SALIN	-0,12	-0,26	0,05	0,08	-0,49	-0,23	-0,43	0,12	0,04	1			
TEMP	0,03	0,08	-0,15	-0,46	-0,18	0,15	-0,10	-0,24	-0,83	-0,18	1		
SECCHI	-0,08	0,01	-0,15	-0,09	-0,23	-0,12	-0,20	-0,33	0,00	0,16	0,10	1	
WIND	0,04	-0,06	0,02	0,01	-0,21	-0,17	-0,21	-0,07	-0,01	0,34	-0,13	0,06	1

P<0.01, R ≥ 0.2752, df=84
P<0.05, R ≥ 0.2120, df=84

A3 1m.

	P-PO4	TP	N-NH4	N-NO2	N-NO3	TN	SiO2	CHLa	OXY	SALIN	TEMP	SECCHI	WIND
P-PO4	1												
TP	0,27	1											
N-NH4	0,13	-0,18	1										
N-NO2	0,20	0,20	0,06	1									
N-NO3	0,02	0,11	-0,01	0,34	1								
TN	-0,12	0,01	-0,14	0,03	0,33	1							
SiO2	0,03	0,14	-0,09	0,43	0,73	0,15	1						
CHLa	-0,05	-0,07	0,07	0,05	0,05	0,01	0,04	1					
OXY	0,03	0,04	0,21	0,32	0,09	-0,18	-0,05	0,11	1				
SALIN	-0,10	-0,12	0,02	0,07	-0,74	-0,30	-0,48	0,07	0,12	1			
TEMP	0,03	-0,08	-0,11	-0,47	-0,07	0,16	0,02	-0,18	-0,86	-0,31	1		
SECCHI	0,07	-0,03	0,03	-0,09	-0,24	-0,30	-0,14	-0,30	-0,03	0,22	0,07	1	
WIND	0,12	-0,14	0,03	0,02	-0,25	-0,09	-0,17	-0,18	-0,01	0,35	-0,12	0,11	1

P<0.01, R ≥ 0.2752, df=84
P<0.05, R ≥ 0.2120, df=84

Table 25

Interestingly, wind intensity and salinity correlated positively at all stations, making in evidence the importance of dominant wind regimes and the ingression of southern water of high salinity and/or enhanced vertical mixing on these stations. Salinity correlated negatively with SiO_2 at stations A0 and A3 and also negatively with N-NO_3 content. Chlorophyll *a* correlated negatively at all stations with Secchi disc depth. High positive correlation coefficients between SiO_2 and N-NO_3 were evidenced at all stations.

2.5. Temporal variations in Timavo River inorganic nutrients and Total Nitrogen and Phosphorus concentrations (2006-2008)

2.5.1. Introduction

Water samples were collected at surface (1m. depth) monthly at two stations located along the final part of Timavo River (Fig. 1), in the period from May 2006 to December 2008. The distance between the two stations was only about 100m and the results presented in this chapter are averaged data from two samples. Salinity was always >0.2psu. In May and July 2006 and in April 2007 only one sample was collected from the River. A total of 61 samples were collected and analyzed for seven environmental parameters: $N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, $P\text{-}PO_4$, SiO_2, Total Nitrogen (TN) and Total Phosphorus (TP).

2.5.2 Methods

For inorganic nutrients ($N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, $P\text{-}PO_4$, SiO_2) determinations, water samples were filtered on GF/F glass fiber filters (0.7µm nominal pore size, 47mm diameter, Whatman International Ltd). TN and TP concentrations were determined using a persulfate digestion procedure (Grasshoff et al. 1983). After the step of digestion, total dissolved nitrogen and phosphorus were determined with the same automated colorimetric methods used for nitrate and reactive phosphorus. Analyses were conducted on a Bran+Luebbe Autoanalyser3 Continuous Flow Analyser (Bran+Luebbe, Norderstedt, Germany) using standard procedures (Bran+Luebbe 2003a,b,c,d,e and references therein). The efficiency of the system was checked before and after sample analyses by replicating calibration standards.

2.5.3. Results

Table 26 shows the descriptive statistics of inorganic nutrients and TN and TP in the period of investigation.

Timavo River							
	$N\text{-}NH_4$ µM	**$N\text{-}NO_2$ µM**	**$N\text{-}NO_3$ µM**	**$P\text{-}PO_4$ µM**	**SiO_2 µM**	**TN µM**	**TP µM**
Max	1.75	0.10	145.69	0.63	65.51	155.47	1.35
Min	0.19	0.01	57.92	0.03	46.49	92.18	0.21
Median	0.93	0.05	110.57	0.13	54.26	121.72	0.59
Average	0.92	0.05	107.71	0.23	55.13	123.79	0.61
Std.Dev.	0.33	0.02	17.59	0.16	5.28	15.96	0.32

Table 26

The descriptive statistics of total and dissolved inorganic nutrient rations are presented in Table 27.

Timavo River	TN:TP	DIN:DIP	Si:DIN	Si:DIP
Max	653	3585	0.93	1781
Min	89	193	0.42	85
Median	213	593	0.50	403
Average	262	793	0.52	400
Std.Dev.	144	654	0.09	317

Table 27

Median dissolved inorganic N:P (DIN:DIP) and Si:DIP ratios resulted to be higher compared to the values found in the Gulf, due to very high N-NO_3 and SiO_2 concentrations in the Timavo River water, making in evidence an strong unbalance compared to the Si:N:P ratio of 15:16:1 suggested by Harrison et al. (1977). Median inorganic Si:DIN ratio resulted to be lower though, because of very high nitrate concentrations.

2.5.4. Timavo River discharge (2006-2008)

Monthly mean Timavo River discharge is showed in Fig. 20. Lowest discharge in the three years of monitoring were like for Isonzo River, generally recorded in the summers; however in 2006 lowest discharge was recorded in October (10.67 m^3s^{-1}), but also July (11.27 m^3s^{-1}), September (12.67 m^3s^{-1}) and November (12.60 m^3s^{-1}) discharge was rather low. Lowest mean monthly discharge in 2007 was recorded in July (9.77 m^3s^{-1}) and August (8.90 m^3s^{-1}), while in 2008, September (11.33 m^3s^{-1}) and October 11.00 m^3s^{-1}) were the "driest" months. Important to note that Timavo River, even in the driest periods, always had an mean monthly discharge above 8.89 m^3s^{-1}, making its outflow to the Gulf of nutrient rich freshwater more constant in time than Isonzo River, which on average has a greater outflow, but suffer in "dry" periods when its discharge to the Gulf nearly stops, like in July 2006 (0.62 m^3s^{-1}) and August 2007 (1.66 m^3s^{-1}). The highest (>25 m^3s^{-1}) monthly mean river discharge in the period of sampling, was in 2006 recorded in May (25.30 m^3s^{-1}) and June (29.79 m^3s^{-1}). In 2007 discharge was highest in January (40.50 m^3s^{-1}) and in February (39.50 m^3s^{-1}). Compared to the two previous years (Tab. 26X), Timavo River discharge was higher in 2008 with mean monthly discharge exceeding 25 m^3s^{-1} in several months; in January (32.79 m^3s^{-1}), March (27.68 m^3s^{-1}), April (56.93 m^3s^{-1}), May (30.14 m^3s^{-1}), November (34.03 m^3s^{-1}) and, like previously seen for Isonzo River, especially in December (92.06 m^3s^{-1}) discharge was high.

In Figure 20 is reported the mean monthly Timavo River discharge into the Gulf for the period of monitoring.

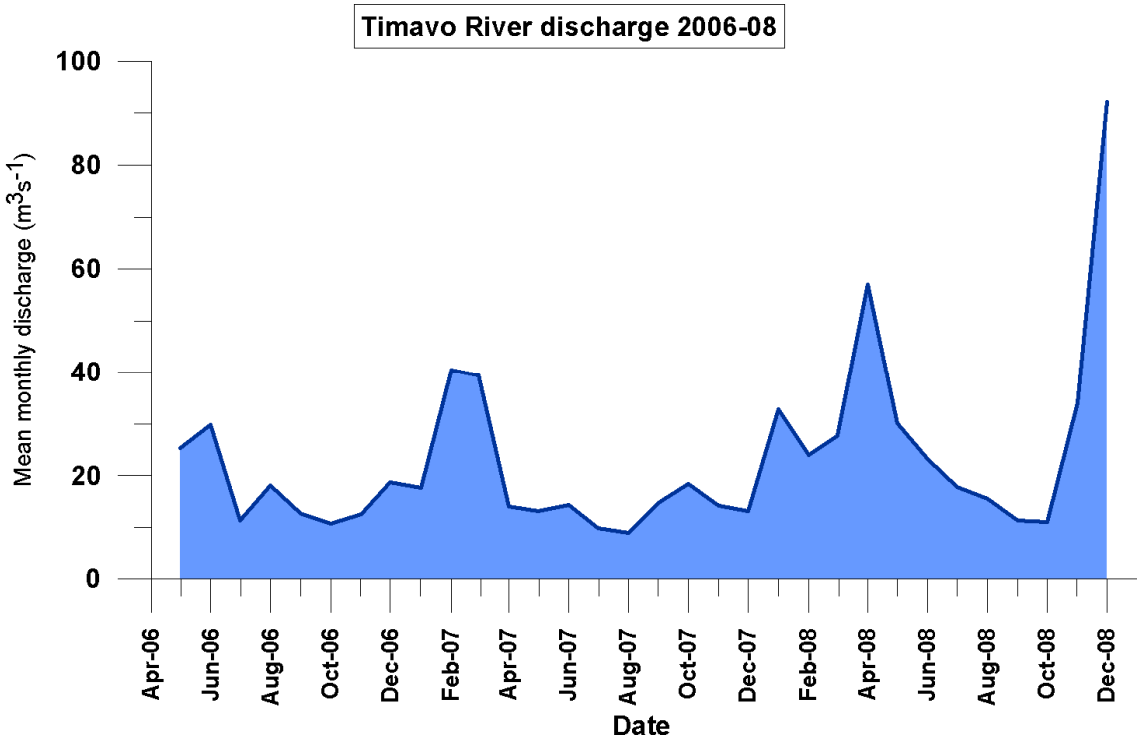

Fig. 20

Descriptive statistics of the mean monthly Timavo River discharge [m^3s^{-1}] are summerised in Tab. 28. In order to be able to compare the mean monthly discharge in the three years, the river discharge from January to April 2006, a period where water sampling did not take place, was included in the construction of the table.

Timavo River			
	2006	**2007**	**2008**
Max	53.13	40.50	92.06
Min	10.67	8.90	11.00
Median	21.99	14.24	25.80
Average	25.68	18.18	31.36
Std.Dev.	14.14	10.54	22.84

Table 28

Overall, 2007 was on average the year with the lowest river outflow and 2008 the year with the highest. Mean discharge for the years 2001-2007 was about 26.73 m^3s^{-1} (ACEGAS-APS S.p.A.).

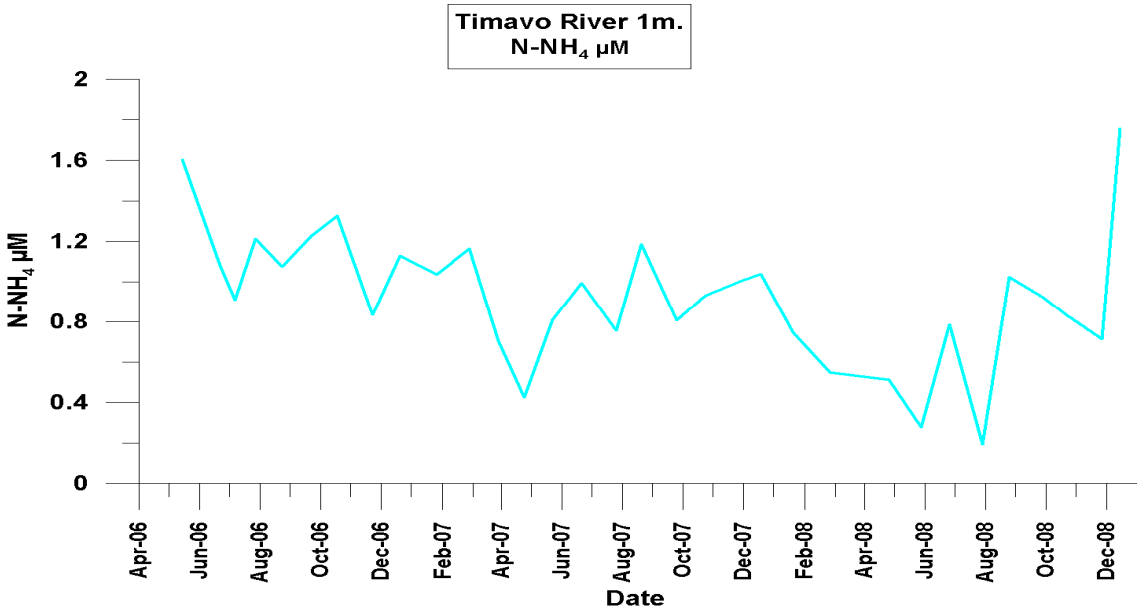

Fig. 21

Ammonium concentrations were lower in the late spring of 2007 and 2008 and in August 2008. Highest concentration was recorded in December 2008 when river discharge was at its highest, however the concentrations recorded are comparable to those found on the different stations in the Gulf.

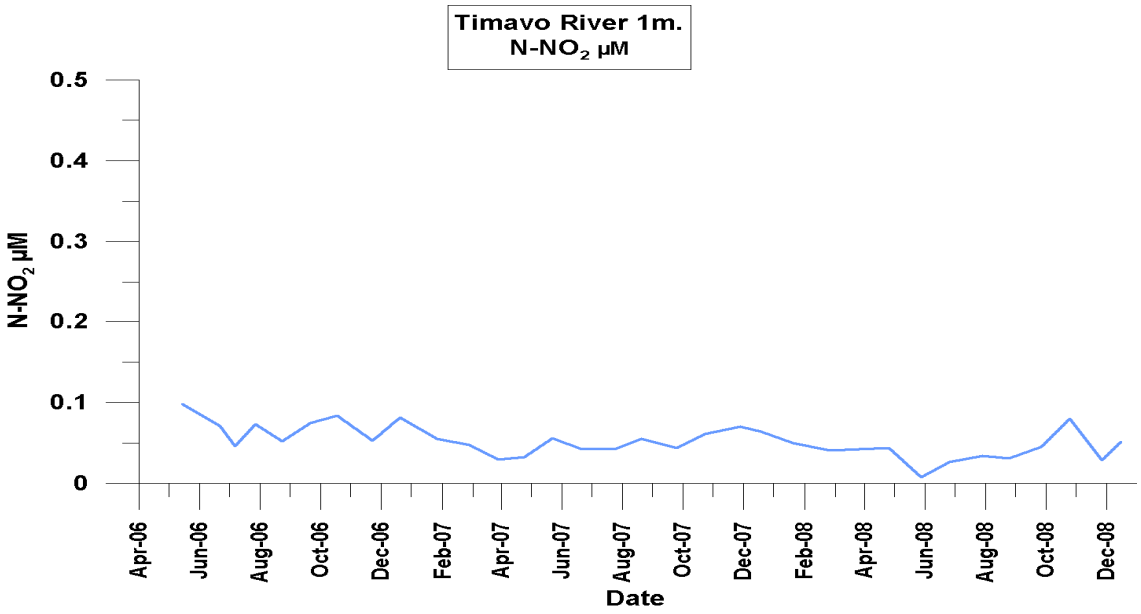

Fig. 22

Nitrite concentrations were always low in the river water and comparable to the concentrations found on the stations in the Gulf. Nitrite winter concentrations were slightly higher than those evidenced in spring.

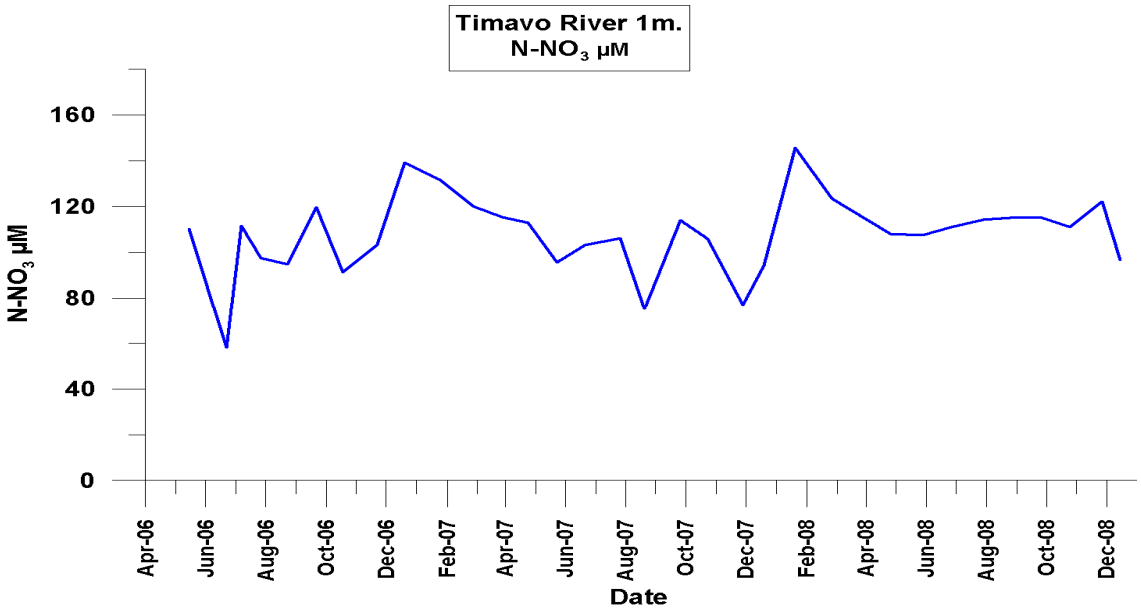

Fig. 23

Nitrate was by far the largest fraction of the dissolved inorganic nitrogen pool, and very high concentrations were recorded in the whole period of monitoring. Nitrate resulted also to be the largest fraction of the Total Nitrogen (TN) pool.

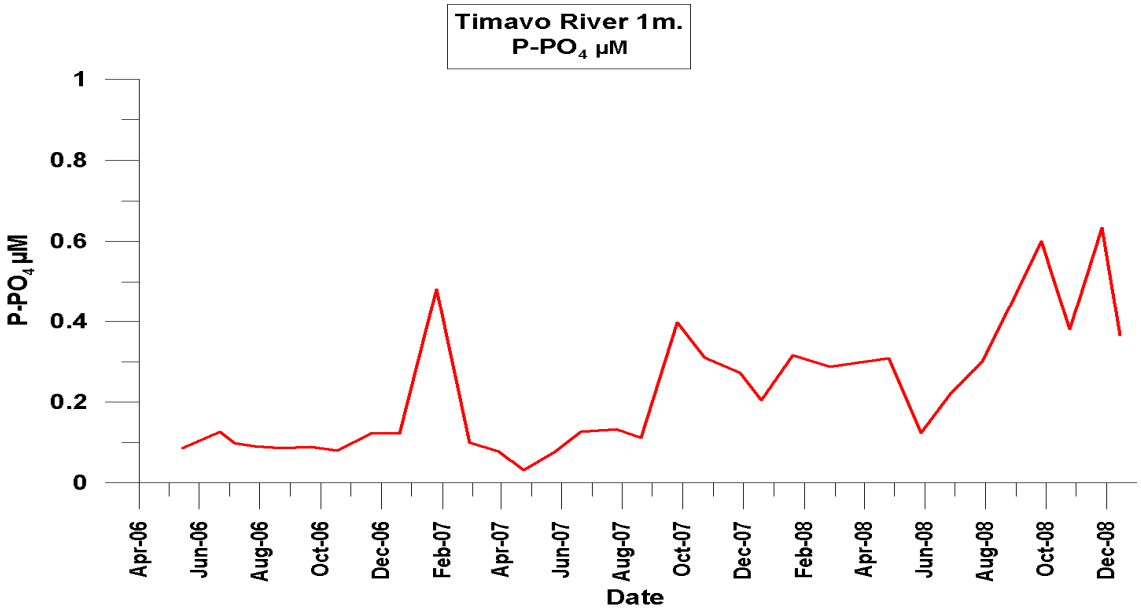

Fig. 24

Phosphate content in the river water varied much in the study period, with generally highest concentrations in autumn and winter and lowest in spring and summer. From August 2007 to December 2008 phosphate content was generally higher. Mean phosphate content calculated for the whole study period resulted to be more than twice that recorded on the sampling stations in the Gulf., making in evidence that, even if the inorganic N:P ratio in river water is unbalanced with respect to the classic Redfield ratio, important amounts of this primary limiting macro nutrient is delivered to the

Gulf by Timavo River.

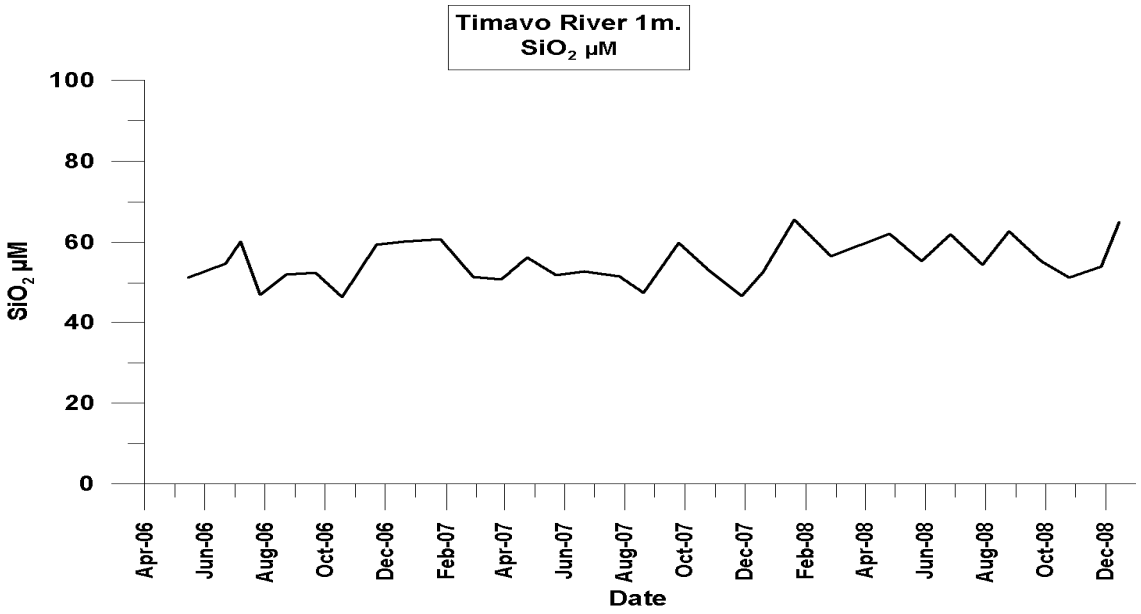

Fig. 25

Silicate concentrations were very high compared to those evidenced in the Gulf, and were rather constant in concentration in the whole study period, making in evidence that Timavo River is an important source of this nutrient to the Gulf.

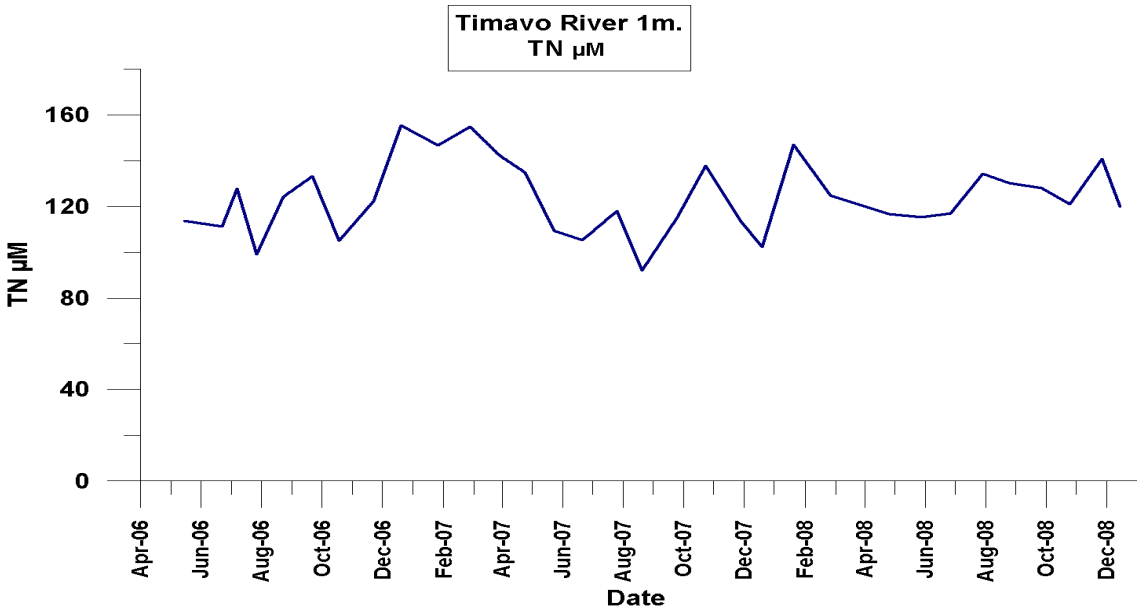

Fig. 26

Highest concentrations of Total Nitrogen were generally recorded in winters, but in 2008 TN concentrations remained always very high, around 120 µM. The largest fraction of TN was constituted by nitrates.

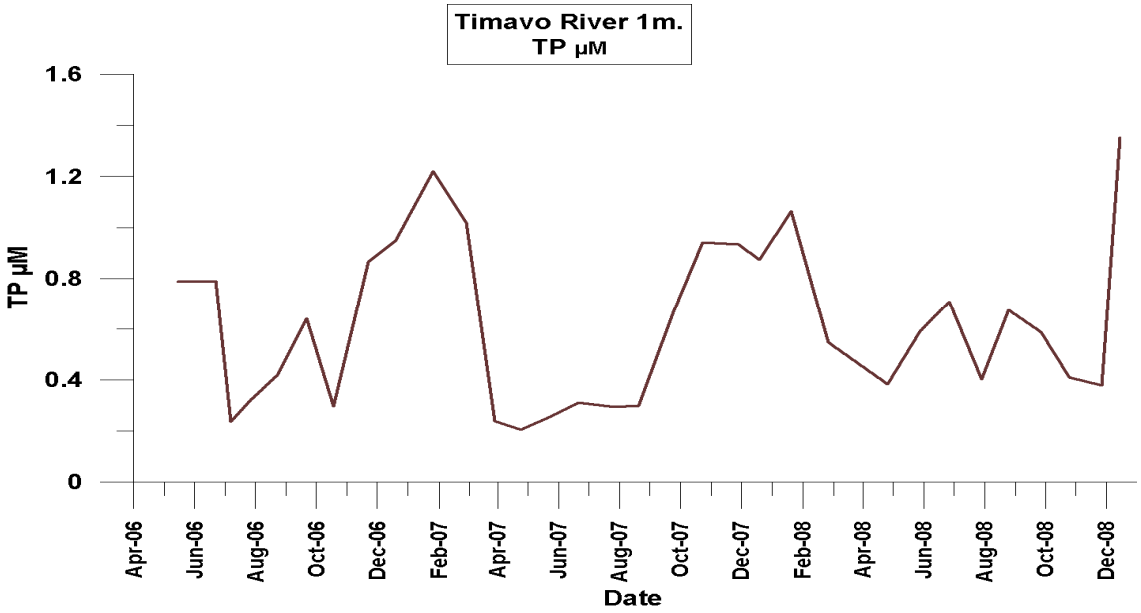

Fig. 27

Among the nutrients considered, Total phosphorus (TP) was the parameter with the most clear monthly trend during the study period, with lowest concentrations in summers and highest in winters. Winter concentrations were very high in all years, reaching 1.35µM during the highest river outflow in December 2008.

2.6. Discussion

The Gulf of Trieste is a highly dynamic system with large spatial and temporal variations in most of the parameters considered. Its geomorphological characteristics and particular hydrology with major freshwater outflow in its shallowest part, together with physical forcing, especially from wind, provide a different picture of each station considered.

Very high DIN:DIP ratios were reached on all stations monitored and significant correlation coefficients between phosphates and salinity were only obtained in the surface water (1m) at station T24 near the Isonzo River mouth, and at station A1, a coastal station near the small town of Muggia (Trieste). Highest median DIN:DIP ratio for the period of investigation was found at station T24 (86), which was mainly due to high N-NO_3 concentrations in low salinity water For a comparison, median Timavo River DIN:DIP ratio reached a value of 593, highlighting that the two main rivers deliver freshwater to the Gulf in excess of inorganic nitrogen to inorganic phosphorus. Station T24 is the northern most station considered in this study, and is also due to its shallowness subject to enhanced vertical mixing, Interestingly, negative correlation coefficients between salinity and DOP were found on 8m on T24 but also at 1m at station T25. On this station was recorded the lowest salinity value (22.43psu) and the highest salinity variations (Tab.1), but the median salinity value was higher than on T24. The fact that DOP correlated with salinity at station T25 (1m) and not at T24 at the same depth could be because of the local hydrology and the nearby submarine wastewater pipeline (Fig.1) of

Monfalcone. Station T23 (1m) was the only station in the central part of the Gulf where a significant negative correlation coefficient between salinity and DOP was evidenced. In accordance with the main direction of surface currents found by Cozzi et al (2008) this could be due to a possible influence from the submarine wastewater pipeline of Trieste. DOP remained on average the major fraction (calculated per year: 56-78%) of the total phosphorus pool in the five years of monitoring, while inorganic P always remained less than 12% and low in concentration, thus indicating biological production in the Gulf is basically dependent on regeneration processes of dissolved organic matter and on pulses of nutrient rich freshwater outflow. Median particulate phosphorus concentrations was also higher on T24 and a negative correlation coefficient between PP and Secchi disc depth was found. Station T03 was station most distant from Isonzo River where salinity values below 30psu were reached. Median Secchi disc depth on T03 was similar to that of station T25, but median DIN:DIP and Si:DIP ratios were much lower (Tab. 12), reaching the ratios determined for the stations more distant from Isonzo River mouth. Regarding the dissolved inorganic nitrogen pool, $N\text{-}NO_3$ remained on average the largest fraction at all stations, however in the central part of the Gulf ammonium concentrations nearly equaled nitrate in concentration, probably as the result of microbial remineralisation processes of organic matter, and only near Isonzo River mouth at station T24 and T25, nitrate resulted to be much higher in concentration. Ammonium concentrations which depend mainly on rimineralization processes did not correlate with surface water salinity on any of the monitored stations. Significant negative correlation coefficients between salinity and nitrates at 1m were found on all stations, except at station T11, but including station A0, A2 and A3, underlining the importance of freshwater outflow of nitrate rich water for the surface concentrations of this nutrient in the Gulf.. The lowest nitrate and nitrite concentrations were recorded in summers, especially in periods of low freshwater input and high water temperature, and were probably due to biological uptake. The temporal variation in nutrients at the stations located near the city of Trieste (A0, A2 and A3) resulted to be similar to the stations in the central part of the Gulf, however, median phosphate content was somewhat higher and DIN:DIP ratios were lower, but considering that the sampling period on these stations was different (2002-2005) from that of other stations in the Gulf (2004-2008), no evident influence from the City of Trieste could be noted. On the other hand, the main direction of surface currents on these stations are NE, so eventually, any signal in nutrient content from the nearby industrial zone of Trieste, or from the Servola wastewater pipeline, would not registered on these station, but rather on the stations like station T23, T22 and perhaps C1, being “down current” to the sources of emission. DON remained, as DOP did for phosphorus, the largest fraction of the total nitrogen pool, however no significant correlation with salinity could be recorded in surface waters on any station, indicating how, in general, this fraction originates in water column and in sediment remineralisation processes and not from river input. In fact, two years of monitoring of Timavo River inorganic and total nitrogen content clearly show, that mathematically, DON cannot be the major fraction of the total nitrogen pool in the river water, because on average, DIN constituted about 88% of TN. Significant correlation coefficients

between Particulate Nitrogen (PN) and salinity was only found at station C1 (1 and 5m) and T22 (1m), but not on any other stations in the gulf. Moreover, significant positive correlations with chlorophyll *a* were evidenced at 1m on T24, T25, T03 and on T22 (18m), indicating a probable biological origin of these PN data.

High correlation coefficients between salinity and SiO2 were found on all stations at 1m, except on T08 and T26 located in the center of the Gulf. Median Si:N ratios varied around the balanced ratio of 0.94 (Harrison et al. 1977) on the stations, with lowest median value on T24 (0.70) and the highest on T26 (1.04). Lowest SiO_2 concentrations were found in the summers, due to low freshwater discharge and phytoplankton uptake. Especially in August 2008 silicate concentration on station C1 dropped to non relievable concentrations (>0.01µM),and on the same date DIN concentrations were also very low, while phosphate concentrations were surprisingly high (FIG), resulting in an totally unbalanced Si:N:P ratio of approx. 0.06:0.68:1, indicating a combined silicate and inorganic nitrogen limitation. But also in September 2008 the DIN:DIP ratio was on average >5.46 on the four sampling depths at C1.

Chapter 3. Evaluating nutrient deficiency of the environment by the determination of ectoenzymatic activities.

3.1. Introduction

A possible indirect way of rapidly evaluating nutrient deficiency of the marine environment is by the determination of ectoenzyme activities. Nutrient limitation may induce microbial cells to synthesize ectoenzymes to enable the acquisition of the limiting nutrient. Ectoenzymes respond rapidly and directly to changes in nutrient availability by manipulating enzyme kinetics to best capitalize environmental conditions. Ectoenzyme activities may thus serve as a proxy for nutrient limitation, not by indicating the amount of the proper substrate present, but by pointing towards the physiological state of the cell or of the total microbial population. Specifically, alkaline phosphatase activity (APA) has been used as an indicator of phosphorous deficiency. It can be synthesized by bacteria and by phytoplankton. Therefore the relative contribution of each group can be inferred from the relationship between population dynamics and phosphorus concentrations. Amino peptidases (AM) hydrolyze peptides and proteins, which comprise a major part (and probably the most utilizable fraction) of the marine organic N pool (Henrichs et al. 1984, Coffin 1989).

Here we studied the nitrogen and phosphorus dynamics in the P-depleted Gulf of Trieste waters. AMA, APA, bacterial biomass, phytoplankton, chlorophyll *a* concentration, temperature, salinity, dissolved inorganic, organic and particulate phosphorus content were analyzed on different timescales in order to study:

- **Inter annual and monthly variation.** Fortnightly sampling, from 13 January 2004 to 11 October 2005 at four depths: 1, 5, 10 and 15m
- **Seasonal and weekly variation**. Sampling on daily basis for one week in four meteorological seasons: Spring (April), Summer (July), Autumn (November 2006) and Winter (March 2007). Sampling was conducted at two depths: 1 and 15m.
- **Diel variation.** Sampling every two hours for 28h. Sampling took place on 8-9'th May 2007 at two depths: 1 and 15m.

These studies were all carried out at coastal station C1.

3.2. Site description

Coastal station C1 (45°42.05'N, 13°42.60'E) within the Marine Reserve of Miramare (Fig. 28), is situated in the Gulf in an area sheltered from boats, fishing and other human activities. Maximum depth at station C1 is 17m.

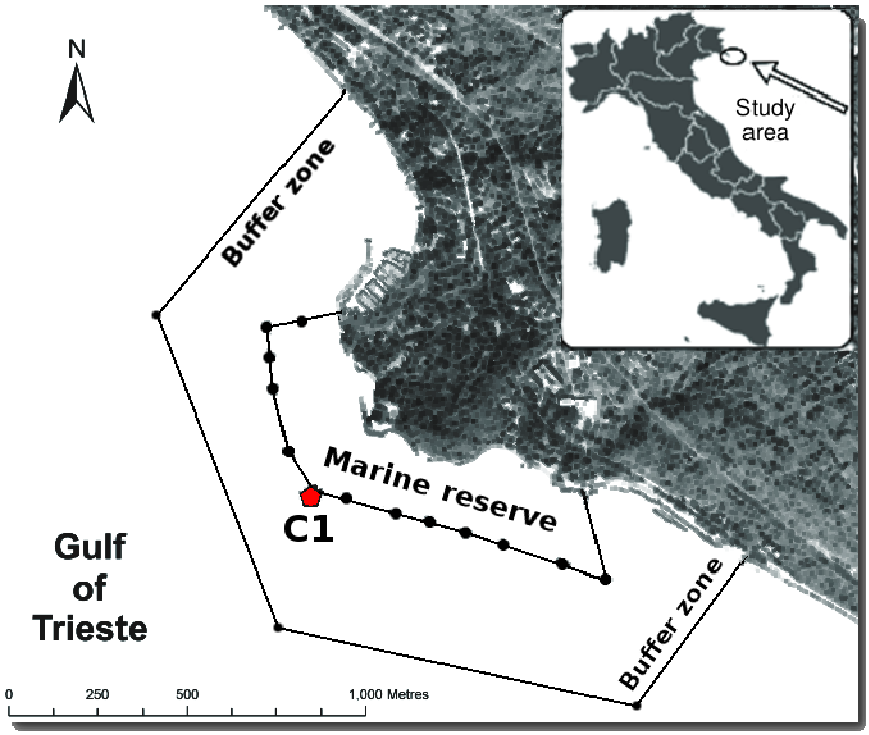

Fig 28.

3.3. Methods

At each sampling, CTD profile was recorded using a Seabird19 Plus multiparametric probe, which was calibrated every 6 months. Salinity was computed, according to the UNESCO formula for salinity determination (UNESCO 1978), from measurements of hydrostatic pressure, temperature and conductivity.

Water samples for the determination of the concentrations of inorganic and organic nutrients, and chlorophyll *a* and for microbial analyses were collected using a 5L Niskin bottle.

For inorganic nutrients ($N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, $P\text{-}PO_4$, SiO_2) and DON and DOP determinations, water samples were filtered on GF/F glass fiber filters (0.7µm nominal pore size, 47mm diameter, Whatman International Ltd). Inorganic nutrient analyses were conducted at room temperature on a five-channel Bran+Luebbe Autoanalyser3 Continuous Flow Analyser (Bran+Luebbe, Norderstedt, Germany), using standard procedures (Bran+Luebbe 2003a,b,c,d,e and references therein). The efficiency of the system was checked before and after sample analyses by replicating calibration standards. DOP and DON concentrations were determined using a UV+H_2O_2 oxidation procedure

(Walsh 1989). After the step of oxidation, total dissolved nitrogen and phosphorus were determined with the same automated colorimetric methods used for nitrate and reactive phosphorus. The concentrations of DON and DOP were calculated as the difference between total dissolved nitrogen and phosphorus and the ambient concentrations of dissolved inorganic nitrogen (calculated as N-NH_4+N-NO_2+N-NO_3) and P-PO_4, respectively.

For Particulate Nitrogen (PN) determination, 250mL of sample were filtered on pre-combusted GF/F glass fiber filter (25mm diameter, Whatman International Ltd) and determined by high temperature oxidation according to Sharp (1974) on a Perkin Elmer 2400 CHNS/O analyzer. For Particulate Phosphorus (PP) determination, water sample (1L) was filtered on pre-combusted GF/F glass fiber filter (25mm diameter, Whatman International Ltd). After high temperature combustion (480°C) in a muffle-oven for 2.5h, PP was extracted from the filter by acid hydrolysis using 1M HCl solution for 24h and subsequently analyzed as P-PO_4 (Solorzano and Sharp 1980).

For chlorophyll *a* determination, aliquots of seawater (1L) were filtered through GF/F glass fiber filter (47mm diameter, Whatman International Ltd). Filters were immediately frozen (-20°C) until analyses. Pigments were extracted overnight in the dark at 4°C with 90% acetone from the homogenate filter and the concentrations were spectrofluorometrically determined following the procedures described by Lorenzen and Jeffrey (1980) using a Perkin Elmer LS50B spectrofluorometer (450nm excitation and 665nm emission wavelengths).

Samples (50mL) taken to estimate heterotrophic and phototrophic picoplankton abundance were fixed with a 2% final concentration formalin (pre-filtered through 0.2µm Acrodisc syringe filter), preserved at 4°C and processed within 48 h. To evaluate the heterotrophic picoplankton abundances, subsamples were stained for 15 min with 4'6 diamidino-2-phenylindole (DAPI, Sigma) at 1µg mL^{-1} final concentration (Porter and Feig 1980), aliquots were filtered in triplicate (1-2 mL subsample) onto 0.2µm pore-size black-stained polycarbonate filters (Ø 25mm, Nuclepore). Filters were mounted on microscope slides using not fluorescent oil (Olympus) and stored at –20°C. Bacterial enumeration was carried out using an Olympus BX 60 F5 epifluorescence microscope equipped with a 100 W high-pressure mercury burner (HPO 100W/2) at 1000X magnification under UV excitation light (BP 330-385, BA 420 nm). At least 20 random fields and a minimum of 300 cells were counted for each filter. Cell counts were converted in carbon concentration using a conversion factor of 20 fg C/cell (Lee and Fuhrman 1987). To evaluate the phototrophic picoplankton abundance samples were filtered onto 0.2µm pore-size black-stained polycarbonate filters (Ø 25mm, Nuclepore). The filters were mounted and microscopically observed using the same procedure described for heterotrophic cells under blue light excitation (BP 420-480 nm, BA 515 nm).

Phytoplankton samples were preserved with hexamethylene tetramine-buffered formalin (1.6% final concentration) at 4°C (Throndsen 1978). Qualitative and quantitative phytoplankton analyses were performed by the Utermöhl (1958) method (Zingone 1990) using an inverted microscope (Zeiss Axiovert 135) equipped with phase contrast.

Hydrolytic enzyme activity was measured with fluorogenic analogs of natural substrates (Hoppe, 1993) derived from 4-methyl-umbelliferone (MUF) and 7-amino-methyl coumarin (AMC). Aminopeptidase activity (AMA) was assayed as the hydrolysis rate of L-leucine-AMC and alkaline phosphatase activity (APA) as the hydrolysis rate of MUF-phosphate. Hydrolysis rate was measured by incubation of 2.5mL subsamples with 200µM (final concentration) leucine-MCA and 50µM (final concentration) MUF-phosphate for 1h in the dark at *in situ* temperature. The fluorescence released by enzymatic cleavage of the artificial substrates was measured fluorometrically, in triplicate, at 380/365 nm excitation and 440/455 nm emission for MUF / AMC substrates using a Shimadzu RF 1501 fluorometer. Standard solutions of MUF and AMC were used to calibrate the fluorometer.

3.4. Inter annual and monthly variation.

Sampling was conducted fortnightly, from 13 January 2004 to 11 October 2005 at four depths: surface, 5m, 10m and 15m . A total of 136 samples were collected and analysed.

3.4.1. Environmental conditions

Descriptive statistics of the main hydrological features at each depth is summerised in Tab. 28.

C1 1m.

	Salinity [psu]	Temperature [°C]	O_2 [ml/L]	Chl *a* [µg/L]
Max	38.36	26.03	6.49	2.28
Min	35.69	6.83	4.72	0.16
Median	37.38	16.97	5.64	0.67
Average	37.34	16.08	5.61	0.73
Std.Dev.	0.69	6.29	0.55	0.45

C1 5m.

	Salinity [psu]	Temperature [°C]	O_2 [ml/L]	Chl *a* [µg/L]
Max	38.36	26.03	6.49	1.95
Min	35.69	6.83	4.72	0.12
Median	37.33	16.99	5.50	0.65
Average	37.34	16.25	5.59	0.70
Std.Dev.	0.68	6.29	0.56	0.40

C1 10 m.

	Salinity [psu]	Temperature [°C]	O_2 [ml/L]	Chl *a* [µg/L]
Max	38.38	25.98	6.64	2.00
Min	36.50	6.75	4.12	0.09
Median	37.67	15.63	5.70	0.70
Average	37.60	15.75	5.60	0.78
Std.Dev.	0.51	6.10	0.65	0.39

C1 15 m.

	Salinity [psu]	Temperature [°C]	O_2 [ml/L]	Chl *a* [µg/L]
Max	38.43	23.32	6.50	2.36
Min	37.02	6.73	3.32	0.21
Median	37.83	14.81	5.64	0.81
Average	37.77	14.86	5.42	0.90
Std.Dev.	0.39	5.53	0.87	0.49

Table 28

Descriptive statistics of the dissolved inorganic, dissolved organic and particulate nutrient fractions at each depth is summerised in Tab. 29.

C1 1m.

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM	PP µM	PN µM
Max	9.31	1.58	11.84	6.93	0.18	6.62	32.11	0.23	7.39
Min	0.04	0.00	0.15	0.43	<0.02	0.27	0.39	0.05	1.41
Median	0.90	0.07	1.28	2.14	0.06	0.61	10.18	0.11	2.66
Average	1.13	0.21	2.26	2.81	0.07	0.91	12.63	0.11	2.98
Std.Dev.	1.53	0.31	2.98	1.70	0.03	1.09	7.84	0.04	1.22

C1 5m.

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM	PP µM	PN µM
Max	1.76	1.93	4.47	5.80	0.14	6.75	121.64	0.25	5.62
Min	<0.03	0.00	0.04	0.20	<0.02	0.24	4.34	0.04	0.99
Median	0.99	0.05	0.91	1.95	0.06	0.61	10.26	0.11	2.89
Average	0.90	0.22	1.25	2.31	0.06	0.90	15.63	0.12	3.08
Std.Dev.	0.50	0.39	1.20	1.35	0.04	1.11	20.44	0.05	1.08

C1 10 m.

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM	PP µM	PN µM
Max	3.58	1.70	4.19	6.16	0.21	4.00	126.47	0.25	5.04
Min	<0.03	0.00	0.02	0.59	<0.02	0.21	2.19	0.06	0.62
Median	0.85	0.06	0.82	2.66	0.06	0.71	9.37	0.12	2.61
Average	0.89	0.25	1.22	2.68	0.07	0.85	13.67	0.12	2.74
Std.Dev.	0.69	0.39	1.20	1.45	0.05	0.70	19.94	0.05	1.05

C1 15 m.

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM	PP µM	PN µM
Max	3.18	3.39	10.68	10.80	0.28	3.66	114.42	1.01	4.13
Min	<0.03	0.00	0.00	1.35	<0.02	0.08	6.23	0.02	0.17
Median	1.01	0.10	0.80	2.78	0.06	0.56	10.83	0.12	2.65
Average	1.15	0.29	1.20	3.21	0.08	0.74	14.79	0.16	2.65
Std.Dev.	0.69	0.59	1.74	1.78	0.05	0.68	17.85	0.16	0.95

Table 29

3.4.2. Enzymatic activities

Alkaline phosphatase activity (APA) varied from 0.28 ± 0.02 nM h^{-1} (13/01/04, 5m) to 192.34 ± 1.47 nM h^{-1} (05/08/04, 5m) during the 22 months of monitoring. The lowest values were detected in winter while higher activity generally corresponded to spring and summer sampling, and to

late summer during 2005. The yearly variation of APA followed to some degree that of dissolved organic phosphorus (DOP) concentration in the water column. This could best be noticed by applying a moving average to the data (Fig. 26).

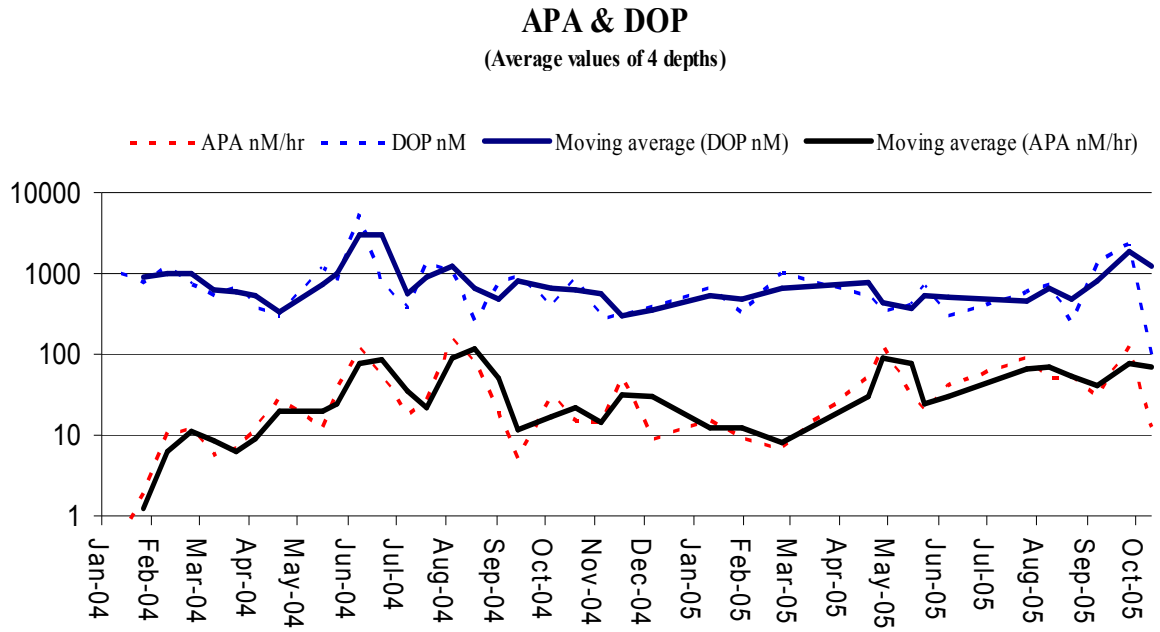

Fig. 29.

No direct correlation between APA and DOP or APA and PO_4 concentration could be evidenced by simple linear regression.

AMA range from 2.06 $\pm$ 0.04 nM h^{-1} (14/09/04, 15m) to 769.62 $\pm$ 4.38 nM h^{-1} (05/08/04, 1m). As for APA, no direct correlation between AMA and DON or AMA and dissolved inorganic nitrogen could be evidenced by simple linear regression. By applying a moving average to the data, no clear trend could be evidenced between AMA and DON (Fig. 30).

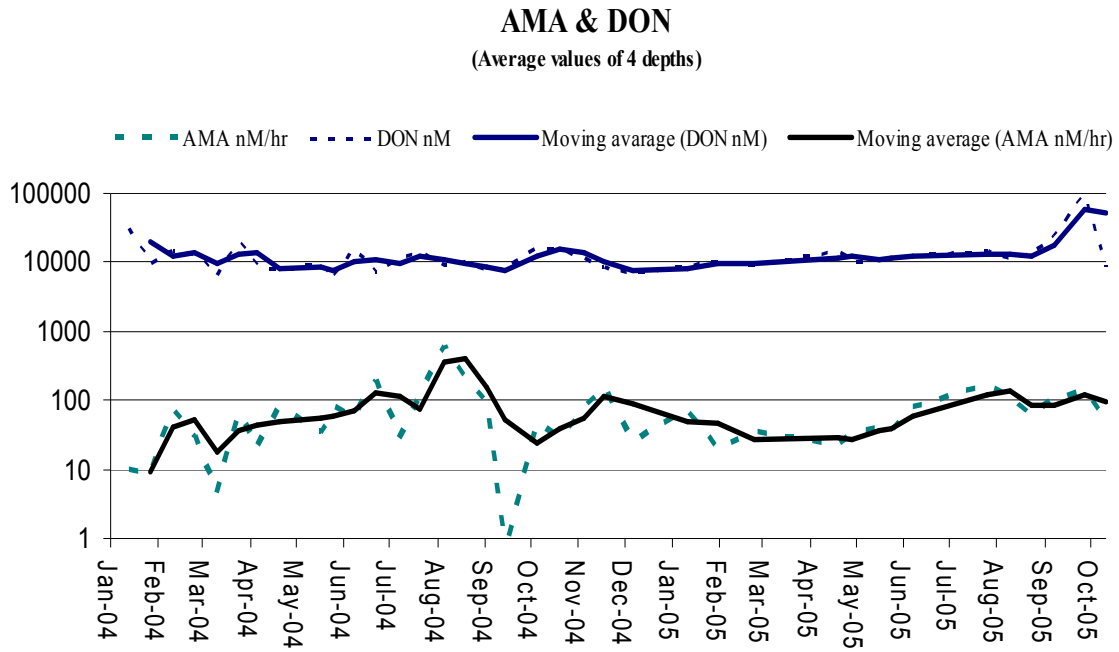

Fig. 30

3.4.3. Principal Component Analysis

Principal Component Analysis (PCA) based on r algorithm (correlation coefficient) was performed using MATEDIT software (Burba et al. 1992). PCA was applied for two main objectives; to discover or to reduce the dimensionality of the data set and to identify new meaningful underlying variables. The data matrix for PCA was constructed as follows: biotic and abiotic variables in rows and samplings dates in columns. From this data matrix a correlation coefficient matrix was calculated among rows. Correlation coefficients corresponding to 5% level of significance were considered and are evidenced in yellow in the cross-correlation tables, while correlation coefficients corresponding to 1% level of significance are reported in cyan. Following variables were considered: Dissolved inorganic nutrients (N-NH_4, N-NO_2, N-NO_3, P-PO_4, SiO_2), dissolved organic nutrients (DON, DOP), Particulate Nitrogen and Phosphorus (PN, PP), alkaline phosphatase activity (APA), aminopeptidase activitity (AMA), heterotrophic picoplankton (HET.PICO), phototrophic picoplankton (PHOT.PICO), Bacillariophyceae, Dinophyceae, other phytoflagellates (OTHER PHYTOFLAG.), total phytoplankton (TOT PHYTOPL.), Chlorophyll a (CHLa), dissolved oxygen (OXY), salinity (SAL), water temperature (TEMP). The PCA was performed on each sampling depth independently. Cross-correlations tables are showed for each sampling depth. Interestingly, APA was strongly and positively correlated with Bacillariophyceae on all but 15m of depth (Tab. 33). APA was correlated with Dinophyceae only at 5m depth. Heterotrophic picoplankton was positively correlated with APA at surface and was the only biological parameter which correlated well with APA at 15m. Phototrophic picoplankton was positively correlated with APA, but only at 10m. Regarding the biogeochemical parameters, APA was positively correlated with dissolved organic phosphorus (DOP) on all but at

15m depth. No correlation between APA and inorganic phosphorus (PO_4) or between APA and particulate phosphorus (PP) could be evidenced. APA was negatively correlated with chlorophyll *a*, but only at 5m depth.

Regarding the physical parameters, APA was negatively well correlated with salinity on all but 15m depth, while it was positively correlated with temperature on all depths. No correlation between APA and oxygen content could be noted. On the other hand, the dissolved organic fraction of Phosphorus (DOP) was positively correlated with Bacillariophyceae on all depths, and very high correlation coefficients were found at surface (0.86), 5m (0,84) and 10m (0,63) depths. DOP correlated well with Dinophyceae only at 5m and with other phytoflagellates only at the surface.

No correlation between P-PO_4 and any biotic parameter could be evidenced, and only a positive correlation between P-PO_4 and salinity at 5m was noticed. Particulate phosphorus (PP) was correlated positively with Chlorophyll *a* and negatively with salinity at the surface level. At 10m depth PP was negatively well correlated with salinity 10m and positively correlated with oxygen content. A very high correlation coefficient (0.85) was found between PP and Dinophyceae at the bottom, while phototrophic picoplankton was positively correlated with PP at 10m.

Aminopeptidase activity (AMA) correlated positively with APA and temperature at all depths, but not with any of the biological parameters considered. AMA was negatively correlated with oxygen at all depth, but 15m, and was negatively correlated with salinity at 10 and 15m. Positive correlation was found between AMA and particulate nitrogen (PN) at 10 and 15m. Phototrophic picoplankton was positively correlated with Dissolved Organic Nitrogen content at 5, 10 and 15m, while heterotrophic picoplankton correlated positively with DON at 10 and 15m.

C1 1m.

	N-NH4	N-NO2	N-NO3	SiO2	P-PO4	DOP	DON	APA	AMA	PP	PN	CHLa	OXY	SALIN	TEMP	HET. PICO	PHOT. PICO	BACILLARIOPHYCEAE	DINOPHYCEAE	OTHER PHYTOFLAG.	TOT. PHYTO
N-NH4	1																				
N-NO2	0.10	1																			
N-NO3	0.04	0.18	1																		
SiO2	-0.03	0.29	0.54	1																	
P-PO4	0.51	0.29	0.07	0.24	1																
DOP	-0.06	-0.11	0.06	-0.14	0.03	1															
DON	0.07	-0.01	-0.13	-0.30	0.12	0.32	1														
APA	-0.12	-0.31	-0.12	-0.08	-0.20	0.33	-0.05	1													
AMA	-0.04	-0.14	-0.01	-0.10	-0.01	0.04	-0.17	0.55	1												
PP	0.20	0.19	0.43	0.51	0.10	0.16	-0.12	0.12	-0.05	1											
PN	0.04	-0.25	0.23	0.28	0.06	0.25	-0.10	0.17	0.11	0.59	1										
CHLa	0.13	0.32	0.49	0.29	0.02	-0.07	0.20	-0.25	-0.31	0.40	0.10	1									
OXY	0.11	0.22	0.24	0.23	0.22	0.06	0.17	-0.28	-0.39	-0.14	-0.13	0.54	1								
SALIN	0.09	0.24	-0.38	-0.29	0.19	-0.28	0.25	-0.48	-0.23	-0.55	-0.38	0.04	0.39	1							
TEMP	-0.08	-0.45	-0.22	-0.26	-0.25	0.10	-0.18	0.47	0.48	0.14	0.28	-0.55	-0.88	-0.55	1						
HET. PICO	-0.15	-0.18	-0.06	-0.01	0.01	0.01	0.23	0.39	0.06	0.05	0.08	-0.19	-0.32	-0.31	0.28	1					
PHOT. PICO	-0.15	-0.19	-0.17	-0.11	-0.04	0.09	-0.06	0.20	0.02	0.29	0.38	-0.28	-0.53	-0.34	0.44	0.57	1				
BACILLARIOPHYCEAE	-0.12	-0.14	-0.03	-0.29	-0.15	0.87	0.31	0.45	0.17	-0.01	0.08	-0.12	-0.01	-0.30	0.21	-0.07	-0.09	1			
DINOPHYCEAE	-0.05	-0.09	0.57	-0.06	-0.22	0.29	0.24	0.01	-0.05	0.21	0.19	0.24	0.10	-0.24	0.00	0.09	0.03	0.31	1		
OTHER PHYTOFLAG.	0.11	-0.23	0.16	0.15	0.01	0.37	0.02	0.16	0.09	0.40	0.48	0.25	0.16	-0.39	0.14	-0.15	0.01	0.29	0.01	1	
TOT. PHYTOPL.	-0.09	-0.19	0.06	-0.23	-0.15	0.88	0.30	0.43	0.17	0.10	0.19	-0.03	0.04	-0.37	0.22	-0.09	-0.08	0.97	0.35	0.48	1

P<0.01, R ≥ 0.4260, df=33
P<0.05, R ≥ 0.3335, df=33

Table 30

C1 5m.

	N-NH4	N-NO2	N-NO3	SiO2	P-PO4	DOP	DON	APA	AMA	PP	PN	CHLa	OXY	SALIN	TEMP	HET. PICO	PHOT. PICO	BACILLARIOPHYCEAE	DINOPHYCEAE	OTHER PHYTOFLAG.	TOT. PHYTO
N-NH4	1																				
N-NO2	0.36	1																			
N-NO3	0.38	0.74	1																		
SiO2	0.27	0.63	0.60	1																	
P-PO4	0.24	0.42	0.35	0.55	1																
DOP	-0.08	-0.14	-0.18	-0.17	-0.05	1															
DON	-0.25	-0.14	-0.19	-0.02	-0.08	0.26	1														
APA	-0.34	-0.32	-0.36	-0.42	-0.31	0.47	0.24	1													
AMA	-0.19	-0.11	-0.12	-0.27	-0.25	0.04	0.08	0.67	1												
PP	0.14	-0.07	-0.11	-0.06	-0.29	0.14	0.25	0.03	-0.07	1											
PN	-0.18	-0.30	-0.36	-0.20	-0.17	0.42	0.38	0.56	0.12	0.26	1										
CHLa	0.19	0.40	0.47	0.28	0.10	-0.08	-0.23	-0.31	-0.26	0.01	-0.03	1									
OXY	0.02	0.12	0.21	-0.04	0.09	0.08	-0.25	-0.27	-0.42	-0.30	-0.27	0.32	1								
SALIN	0.03	0.16	0.03	0.10	0.39	-0.23	-0.08	-0.49	-0.29	-0.24	-0.49	0.01	0.39	1							
TEMP	-0.19	-0.37	-0.46	-0.22	-0.25	0.07	0.19	0.53	0.52	0.24	0.44	-0.40	-0.89	-0.55	1						
HET. PICO	-0.16	-0.09	-0.07	0.00	0.00	0.07	0.52	0.30	0.14	0.22	0.25	-0.37	-0.38	-0.21	0.30	1					
PHOT. PICO	-0.11	-0.21	-0.22	0.00	-0.14	0.05	0.65	0.19	0.10	0.26	0.37	-0.23	-0.57	-0.36	0.54	0.44	1				
BACILLARIOPHYCEAE	-0.15	-0.08	-0.08	-0.19	-0.05	0.85	-0.03	0.46	0.10	0.05	0.35	0.05	0.13	-0.19	0.04	-0.08	-0.09	1			
DINOPHYCEAE	0.12	-0.34	-0.30	-0.33	-0.31	0.42	0.17	0.39	0.13	0.29	0.67	-0.06	-0.21	-0.43	0.41	0.21	0.36	0.37	1		
OTHER PHYTOFLAG.	0.03	-0.27	-0.23	-0.22	-0.20	0.28	-0.05	0.27	0.07	0.19	0.42	0.35	0.06	-0.44	0.20	-0.24	0.12	0.22	0.47	1	
TOT. PHYTOPL.	-0.13	-0.13	-0.12	-0.22	-0.09	0.85	-0.04	0.49	0.11	0.08	0.41	0.10	0.13	-0.25	0.07	-0.11	-0.06	0.99	0.45	0.37	1

P<0.01, R ≥ 0.42030, df=34
P<0.05, R ≥ 0.32876, df=34

Table 31

C1 10m.

	N-NH4	N-NO2	N-NO3	SiO2	P-PO4	DOP	DON	APA	AMA	PP	PN	CHLA	OXY	SALIN	TEMP	HET. PICO	PHOT. PICO	BACILLARIOPHYCEAE	DINOPHYCEAE	OTHER PHYTOFLAG.	TOT. PHYTO
N-NH4	1																				
N-NO2	0.25	1																			
N-NO3	0.24	0.78	1																		
SiO2	0.50	0.64	0.57	1																	
P-PO4	0.35	0.42	0.46	0.59	1																
DOP	-0.07	-0.19	-0.21	-0.24	-0.04	1															
DON	-0.19	-0.08	-0.10	-0.08	0.28	0.36	1														
APA	-0.14	-0.32	-0.40	-0.49	-0.12	0.42	0.42	1													
AMA	0.03	-0.10	-0.15	-0.25	0.02	0.04	0.07	0.62	1												
PP	0.53	-0.05	-0.09	0.25	0.03	0.06	0.05	0.16	0.26	1											
PN	0.01	-0.31	-0.35	-0.23	-0.15	0.17	0.16	0.45	0.38	0.49	1										
CHLA	0.07	0.17	0.12	-0.02	-0.21	-0.11	-0.17	-0.24	-0.21	0.05	0.14	1									
OXY	-0.40	-0.01	0.01	-0.16	-0.23	0.08	-0.16	-0.16	-0.36	-0.55	-0.12	0.19	1								
SALIN	-0.21	0.08	0.12	0.06	0.14	-0.08	-0.20	-0.48	-0.39	-0.40	-0.29	0.07	0.57	1							
TEMP	0.17	-0.32	-0.38	-0.23	-0.14	0.04	0.16	0.45	0.49	0.53	0.34	-0.24	-0.83	-0.717674	1						
HET. PICO	-0.08	-0.13	-0.03	-0.08	0.25	0.11	0.52	0.34	0.19	0.26	0.44	-0.18	-0.36	-0.14	0.38	1					
PHOT. PICO	0.07	-0.20	-0.18	0.00	0.08	0.16	0.64	0.34	0.15	0.37	0.29	-0.22	-0.62	-0.50	0.60	0.55	1				
BACILLARIOPHYCEAE	-0.14	-0.09	-0.09	-0.24	-0.10	0.65	0.07	0.37	0.12	0.00	0.20	-0.19	0.13	-0.05	-0.03	-0.09	-0.03	1			
DINOPHYCEAE	-0.05	-0.36	-0.28	-0.39	-0.21	0.12	0.01	0.17	0.22	0.01	0.47	0.04	-0.11	-0.14	0.28	0.19	0.24	0.03	1		
OTHER PHYTOFLAG.	0.16	-0.23	-0.24	-0.22	-0.33	0.05	-0.17	0.14	0.14	-0.03	0.22	0.08	0.13	-0.35	0.11	-0.34	-0.01	-0.04	0.49	1	
TOT. PHYTOPL.	-0.11	-0.15	-0.14	-0.29	-0.17	0.65	0.04	0.40	0.15	-0.01	0.25	-0.17	0.15	-0.12	0.00	-0.14	-0.02	0.98	0.16	0.17	1

P<0.01, R ≥ 0.4203, df=34
P<0.05, R ≥ 0.3288, df=34

Table 32

C1 15m.

	N-NH4	N-NO2	N-NO3	SiO2	P-PO4	DOP	DON	APA	AMA	PP	PN	CHLA	OXY	SALIN	TEMP	HET. PICO	PHOT. PICO	BACILLARIOPHYCEAE	DINOPHYCEAE	OTHER PHYTOFLAG.	TOT. PHYTO
N-NH4	1																				
N-NO2	-0.01	1																			
N-NO3	-0.02	0.95	1																		
SiO2	0.33	0.73	0.74	1																	
P-PO4	0.11	0.65	0.66	0.77	1																
DOP	-0.03	-0.19	-0.22	-0.10	-0.11	1															
DON	-0.18	-0.07	-0.07	-0.02	0.06	0.38	1														
APA	-0.11	-0.24	-0.29	-0.18	-0.26	0.25	0.43	1													
AMA	0.04	-0.06	-0.11	-0.12	-0.17	0.10	0.03	0.52	1												
PP	0.23	-0.15	-0.16	-0.10	-0.02	-0.03	0.04	0.16	0.28	1											
PN	0.20	-0.31	-0.35	-0.11	-0.45	0.21	-0.02	0.33	0.35	0.18	1										
CHLA	0.10	-0.14	-0.19	-0.29	-0.39	-0.15	-0.19	-0.13	0.02	0.18	0.35	1									
OXY	-0.61	-0.22	-0.23	-0.56	-0.25	-0.12	-0.10	-0.11	-0.24	-0.25	-0.27	0.04	1								
SALIN	-0.33	-0.21	-0.19	-0.25	0.01	-0.09	-0.03	-0.09	-0.33	-0.14	-0.47	-0.06	0.55	1							
TEMP	0.41	-0.06	-0.07	0.25	-0.06	0.27	0.15	0.36	0.46	0.33	0.59	-0.02	-0.82	-0.69	1						
HET. PICO	0.15	-0.07	-0.05	0.20	0.05	0.01	0.38	0.47	0.14	-0.01	0.23	-0.19	-0.31	0.03	0.31	1					
PHOT. PICO	0.12	-0.09	-0.09	0.10	-0.14	0.28	0.42	0.16	0.00	0.00	0.31	-0.10	-0.50	-0.57	0.62	0.23	1				
BACILLARIOPHYCEAE	-0.13	-0.08	-0.08	-0.20	-0.20	0.35	-0.01	0.03	0.18	-0.09	0.02	0.12	0.09	0.16	-0.11	-0.06	-0.16	1			
DINOPHYCEAE	0.03	-0.11	-0.11	-0.25	-0.08	-0.13	0.04	0.08	0.13	0.85	-0.01	0.25	0.04	0.10	0.00	-0.03	-0.15	0.06	1		
OTHER PHYTOFLAG.	0.07	-0.17	-0.18	-0.29	-0.22	0.15	-0.21	0.01	0.19	-0.02	0.24	0.01	0.16	-0.28	0.07	-0.39	0.06	-0.12	0.01	1	
TOT. PHYTOPL.	-0.10	-0.14	-0.14	-0.30	-0.26	0.35	-0.06	0.04	0.24	0.04	0.08	0.16	0.13	0.10	-0.09	-0.16	-0.16	0.95	0.22	0.14	1

P<0.01, R ≥ 0.4203, df=34
P<0.05, R ≥ 0.3288, df=34

Table 33

3.5. Seasonal and weekly variation.

3.5.1. Introduction

Sampling took place on daily basis for one week in four meteorological seasons: Spring (April), Summer (July), Autumn (November 2006) and Winter (March 2007). Surface and bottom layer were sampled. Phytoplankton community was not analyzed.

3.5.2. Results

The descriptive statistics of the main hydrological features registered in each meteorological season are summarized in Table 34.

C1 1m. "Spring"

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Chl *a* [µg/L]	APA [nM h^{-1}]	AMA [nM h^{-1}]
Max	37.55	10.11	6.86	0.63	11.13	37.64
Min	35.24	8.90	5.30	0.06	1.39	6.66
Median	36.92	9.72	6.68	0.21	6.56	20.81
Average	36.76	9.63	6.51	0.24	6.23	21.61
Std.Dev.	0.80	0.51	0.54	0.18	4.54	11.01

C1 15m. "Spring"

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Chl *a* [µg/L]	APA [nM h^{-1}]	AMA [nM h^{-1}]
Max	37.95	9.14	6.90	1.14	16.74	25.33
Min	37.57	8.08	6.63	0.29	2.64	9.95
Median	37.74	8.70	6.68	0.50	6.62	18.75
Average	37.73	8.68	6.70	0.61	7.31	16.70
Std.Dev.	0.13	0.32	0.09	0.32	4.88	5.89

C1 1m. "Summer"

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Chl *a* [µg/L]	APA [nM h^{-1}]	AMA [nM h^{-1}]
Max	37.48	23.76	5.62	0.75	1585.49	124.51
Min	36.04	20.84	4.06	0.34	44.59	53.68
Median	37.26	22.09	5.45	0.55	64.07	75.35
Average	37.13	22.06	5.29	0.54	325.92	87.83
Std.Dev.	0.49	0.96	0.55	0.18	570.34	30.11

C1 15m. "Summer"

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Chl *a* [µg/L]	APA [nM h^{-1}]	AMA [nM h^{-1}]
Max	20.23	37.61	6.02	2.41	96.05	191.39
Min	18.30	37.50	5.64	0.59	25.39	42.27
Median	19.25	37.58	5.87	1.29	54.28	109.64
Average	19.22	37.56	5.86	1.50	62.48	108.57
Std.Dev.	0.82	0.04	0.14	0.84	28.77	60.51

C1 1m. "Autumn"

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Chl *a* [µg/L]	APA [nM h^{-1}]	AMA [nM h^{-1}]
Max	37.37	17.38	5.52	1.24	119.47	131.48
Min	37.33	16.40	5.25	0.35	25.24	66.96
Median	37.35	16.86	5.45	0.46	47.75	89.82
Average	37.35	16.82	5.43	0.61	58.3	93.74
Std.Dev.	0.01	0.33	0.09	0.32	30.64	22.38

C1 15m. "Autumn"

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Chl *a* [µg/L]	APA [nM h^{-1}]	AMA [nM h^{-1}]
Max	37.37	17.11	5.50	1.18	47.46	134.63
Min	37.34	16.27	5.10	0.30	27.20	67.89
Median	37.35	16.67	5.40	0.60	42.50	99.23
Average	37.35	16.67	5.36	0.64	39.45	96.99
Std.Dev.	0.01	0.29	0.15	0.32	8.67	23.97

C1 1m. "Winter"

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Chl *a* [µg/L]	APA [nM h^{-1}]	AMA [nM h^{-1}]
Max	37.34	11.61	8.17	0.67	127.15	56.61
Min	36.83	11.31	5.94	0.09	17.28	24.57
Median	37.09	11.39	5.99	0.38	21.85	29.06
Average	37.11	11.44	6.73	0.41	47.45	38.29
Std.Dev.	0.20	0.12	1.06	0.24	46.33	16.07

C1 15m. "Winter"

	Salinity [psu]	Temperature [°C]	O_2 [mL/L]	Chl *a* [µg/L]	APA [nM h^{-1}]	AMA [nM h^{-1}]
Max	37.48	11.69	8.59	0.54	138.46	53.34
Min	37.19	11.16	5.79	0.15	9.58	23.77
Median	37.40	11.46	6.12	0.36	20.73	26.63
Average	37.34	11.47	6.92	0.35	45.94	33.61
Std.Dev.	0.14	0.21	1.33	0.16	53.46	12.35

Table 34

Descriptive statistics of the dissolved inorganic, dissolved organic nutrient fractions in each meteorological season `is summerised in Tab. 35.

C1 1m. "Spring"

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM
Max	1.05	0.16	11.31	7.61	0.08	0.26	15.58
Min	0.03	0.02	1.45	3.14	0.03	0.02	7.04
Median	0.46	0.09	5.98	4.81	0.07	0.12	9.52
Average	0.54	0.09	5.67	5.13	0.06	0.13	10.44
Std.Dev.	0.39	0.05	3.57	1.59	0.02	0.08	2.75

C1 15m. "Spring"

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM
Max	0.64	0.10	2.63	5.63	0.09	0.20	13.19
Min	0.14	0.03	1.03	2.38	0.04	0.04	6.02
Median	0.43	0.07	1.50	3.61	0.07	0.09	8.61
Average	0.39	0.07	1.81	3.70	0.07	0.10	9.62
Std.Dev.	0.22	0.02	0.61	0.99	0.02	0.05	2.54

C1 1m. "Summer"

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM
Max	1.50	0.04	3.15	0.94	0.05	0.62	29.32
Min	1.16	0.01	0.36	0.44	0.02	0.31	7.27
Median	1.20	0.02	0.56	0.59	0.03	0.45	11.49
Average	1.29	0.02	1.10	0.64	0.03	0.44	13.83
Std.Dev.	0.15	0.02	1.09	0.16	0.01	0.09	7.56

C1 15m. "Summer"

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM
Max	2.18	0.04	3.28	1.06	0.04	0.86	21.16
Min	1.05	0.00	0.32	0.18	0.03	0.26	6.14
Median	1.23	0.01	0.72	0.50	0.03	0.53	10.73
Average	1.40	0.02	1.46	0.52	0.03	0.54	11.89
Std.Dev.	0.45	0.02	1.34	0.34	0.01	0.22	5.56

C1 1m. "Autumn"

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM
Max	2.81	0.20	9.94	5.11	0.15	0.43	77.59
Min	1.17	0.06	0.88	1.86	0.02	<0.02	8.08
Median	1.71	0.11	1.23	2.52	0.08	0.13	12.83
Average	1.79	0.11	4.06	2.99	0.08	0.16	21.38
Std.Dev.	0.54	0.05	3.94	1.2	0.05	0.15	25.11

C1 15m. "Autumn"

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM
Max	2.48	0.18	3.98	3.40	0.10	0.31	31.36
Min	1.47	0.09	0.99	1.47	< 0.02	0.05	7.53
Median	1.78	0.12	2.01	2.48	0.05	0.14	10.44
Average	1.86	0.13	2.29	2.46	0.05	0.17	13.16
Std.Dev.	0.35	0.03	1.38	0.73	0.04	0.10	9.02

C1 1m. "Winter"

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM
Max	1.58	0.31	4.39	16.05	0.08	0.11	12.33
Min	0.22	0.12	0.30	3.67	0.02	0.02	6.29
Median	1.48	0.23	2.77	4.66	0.05	0.08	8.53
Average	1.18	0.23	2.67	6.77	0.05	0.08	8.72
Std.Dev.	0.56	0.08	1.65	5.22	0.02	0.04	2.24

C1 15m. "Winter"

	$N\text{-}NH_4$ µM	$N\text{-}NO_2$ µM	$N\text{-}NO_3$ µM	SiO_2 µM	$P\text{-}PO_4$ µM	DOP µM	DON µM
Max	2.59	0.36	4.29	6.26	0.12	0.08	10.57
Min	0.31	0.15	0.78	0.67	< 0.02	< 0.02	6.40
Median	1.66	0.27	2.50	4.67	0.07	0.02	8.42
Average	1.54	0.28	2.60	4.26	0.07	0.03	8.40
Std.Dev.	0.82	0.08	1.30	2.12	0.04	0.04	1.50

Table 35

The lowest APA rates were evidenced in Spring 2006 at both depths, while the highest rates were evidenced in Summer. During Spring sampling period the mean temperature value was lesser than during Winter and also Chlorophyll concentration was very low. No phytoplankton spring bloom was detected. Even if direct correlation between APA and DOP or APA and phosphate concentration could be evidenced by simple linear regression, the highest DOP concentrations were found during Summer at both depths when APA rates were the highest. The $P\text{-}PO_4$ concentrations were low in all seasons. Correlations were found between APA rate and physical parameters such as temperature, conductivity and oxygen content (data not shown).

The lowest AM activities were, as for APA, evidenced in Spring while the highest were found in Autumn at the surface and in Summer at the bottom. In Autumn the water temperature in November 2006 was particularly high, around 16.6°C. Moreover, simple linear regression showed that AMA rates correlated with physical parameters in the same way as APA. In addition, AMA correlated positively with DIN in Spring , but only at 15m.

3.5.3. Principal Component Analysis

PCA was carried out according to the same methods and principles previously described in chapter 3.3.1. The following variables were considered: dissolved inorganic nutrients ($N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, $P\text{-}PO_4$, SiO_2), dissolved organic nutrients (DON, DOP), heterotrophic picoplankton (HET.PICO), Chlorophyll *a* (CHLa), dissolved oxygen (OXY), salinity (SAL), water temperature (TEMP). The PCA was, as before, performed on each sampling depth independently but considering all data collected (4 weekly experiments). Correlation coefficients corresponding to 5% level of significance were considered and are evidenced in yellow in the cross-correlation tables, while correlation coefficients corresponding to 1% level of significance are reported in cyan.

C1 1m.

	N-NH4	N-NO2	N-NO3	SiO2	P-PO4	DOP	DON	DIN	APA	AMA	CHLa	OXY	SALIN	TEMP	HET. PICO	PHOT. PICO
N-NH4	1															
N-NO2	0.13	1														
N-NO3	0.01	0.43	1													
SiO2	-0.44	0.43	0.28	1												
P-PO4	0.07	0.48	0.55	0.09	1											
DOP	0.19	-0.51	-0.16	-0.49	-0.35	1										
DON	0.54	-0.05	0.29	-0.14	-0.07	0.22	1									
DIN	0.19	0.47	0.98	0.20	0.56	-0.13	0.38	1								
APA	0.13	-0.26	-0.23	-0.27	-0.19	0.33	-0.08	-0.21	1							
AMA	0.47	-0.26	-0.27	-0.54	0.01	0.41	0.16	-0.18	0.09	1						
CHLa	0.33	-0.04	-0.24	-0.29	-0.08	0.18	0.12	-0.18	0.23	0.53	1					
OXY	-0.42	0.43	0.18	0.35	0.16	-0.44	-0.30	0.11	-0.16	-0.55	-0.35	1				
SALIN	0.25	-0.14	-0.49	-0.27	0.03	0.02	0.06	-0.44	0.02	0.24	0.08	0.02	1			
TEMP	0.46	-0.52	-0.40	-0.65	-0.28	0.75	0.17	-0.32	0.40	0.75	0.45	-0.69	0.20	1		
HET. PICO	0.11	-0.38	-0.07	-0.38	-0.13	0.58	0.05	-0.05	0.09	0.60	0.08	-0.31	-0.25	0.55	1	
PHOT. PICO	-0.17	-0.57	-0.15	-0.35	-0.37	0.58	-0.09	-0.19	0.64	-0.04	0.11	-0.31	-0.29	0.38	0.20	1

P<0.01, R ≥ 0.4905, df=24
P<0.05, R ≥ 0.3876, df=24

Table 36

C1 15m.

	N-NH4	N-NO2	N-NO3	SiO2	P-PO4	DOP	DON	DIN	APA	AMA	CHLa	OXY	SALIN	TEMP	HET. PICO	PHOT. PICO
N-NH4	1															
N-NO2	0.44	1														
N-NO3	0.40	0.45	1													
SiO2	0.02	0.69	0.41	1												
P-PO4	0.07	0.50	0.61	0.65	1											
DOP	0.07	-0.57	-0.15	-0.66	-0.45	1										
DON	0.23	-0.17	-0.09	-0.33	-0.16	0.03	1									
DIN	0.75	0.57	0.90	0.34	0.49	-0.11	0.03	1								
APA	0.39	0.06	0.05	-0.22	-0.17	0.34	0.09	0.21	1							
AMA	0.53	-0.22	-0.16	-0.54	-0.33	0.44	0.32	0.11	0.55	1						
CHLa	-0.01	-0.47	-0.28	-0.55	-0.33	0.62	0.26	-0.23	0.46	0.66	1					
OXY	-0.25	0.33	0.28	0.57	0.32	-0.37	-0.25	0.10	0.10	-0.53	-0.19	1				
SALIN	-0.61	-0.48	-0.19	0.05	0.22	0.07	-0.07	-0.44	-0.33	-0.32	0.14	0.33	1			
TEMP	0.59	-0.27	-0.06	-0.69	-0.43	0.71	0.23	0.21	0.52	0.81	0.50	-0.62	-0.41	1		
HET. PICO	-0.10	-0.52	-0.11	-0.51	-0.23	0.69	0.12	-0.15	0.24	0.52	0.66	-0.43	0.13	0.50	1	
PHOT. PICO	-0.65	-0.49	-0.27	0.07	-0.03	0.14	-0.16	-0.51	-0.44	-0.42	0.07	0.18	0.76	-0.38	0.28	1

P<0.01, R ≥ 0.5194, df=21
P<0.05, R ≥ 0.4125, df=21

Table 37

A highly significant correlation coefficient was found between APA and phototrophic picoplankton at surface level, while heterotrophic picoplankton was positively correlated with AMA at the same depth suggesting a different behavior of prokaryotic communities. High positive correlation coefficients were evidenced between DOP and picoplankton, both phototrophic and heterotrophic. At 15m phototrophic picoplankton correlated negatively with APA and AMA, while heterotrophic picoplankton correlated positively with AMA and DOP. Interestingly DOP correlated well with AMA as at 1m, but on the other hand, APA correlated with AMA which was not the case at 1m.

3.6. Diel variation

Sampling took place every two hours for 28h at station C1 on 8-9'th May 2007. Seawater was collected at surface and near the bottom (15m).

3.6.1. Results

Alkaline phosphatase activity varied lesser at surface than at 15m, and the average surface value was slightly higher (131nM/h^{-1}) than the bottom value (101nM/h^{-1}), because it remained comparatively higher at surface on the 9'th May. At the bottom, the highest APA was registered at noon on 8'th May and during the night, while the lowest APA was evidenced at ten o'clock on 9'th. Positive correlation by simple linear regression between APA and DOP was evidenced only at 15m, while a week positive correlation was found between APA and P-PO_4 content at 1m. Phosphate concentrations were always very low at both depths. A positive correlation between APA and O_2 content was also evidenced at 15m, but not at 1m. No correlation could be evidenced between APA and temperature or between APA and chlorophyll *a*. This could be due to only small diurnal variations in temperature and evidence that phytoplankton apparently did not release APA. Average water temperature at 1m was 18.7°C while it was only somewhat lower at 15m reaching 16.9°C.

Aminopeptidase activity was on average slightly higher at 1m (187 nM/h^{-1}) than at 15m (138 nM/h^{-1}), but varied much in the same way on both depths, with highest rates in the noon and at night, and lowest around ten o'clock on 9'th May. A positive but weak correlation between AMA and DON was

found by simple linear regression at 1m, while AMA and dissolved inorganic nitrogen correlated positively much better at this depth. A positive correlation between AMA and O_2 content was also evidenced at 1m, but was weaker at 15m. As for APA, no correlation could be evidenced between AMA and temperature or between AMA and chlorophyll *a*, however a negative correlation between AMA and salinity was evidenced, but only at 1m.

3.6.2. Principal Component Analysis

Cross correlation of surface data (1m) made in evidence a positive correlation between APA and P-PO_4, but APA did not correlate well with any other chemical, physical or biological parameter at this depth. However, APA correlated positively with ammonium, negatively with silicate and positively with DOP at 15m.

C1 1m.

	N-NH4	N-NO2	N-NO3	SiO2	P-PO4	DOP	DON	DIN	APA	AMA	CHLa	OXY	SALIN	TEMP	HET. PICO	PHOT. PICO
N-NH4	1															
N-NO2	0.40	1														
N-NO3	0.53	0.94	1													
SiO2	0.72	0.83	0.93	1												
P-PO4	0.13	0.72	0.67	0.64	1											
DOP	0.68	0.27	0.33	0.49	-0.03	1										
DON	0.16	0.38	0.26	0.25	0.14	0.33	1									
DIN	0.56	0.93	1.00	0.94	0.66	0.35	0.26	1								
APA	0.05	0.23	0.43	0.48	0.55	0.10	-0.03	0.42	1							
AMA	0.38	0.75	0.82	0.76	0.54	0.32	0.51	0.81	0.48	1						
CHLa	0.32	0.30	0.24	0.26	-0.01	0.48	0.33	0.25	-0.09	0.41	1					
OXY	0.33	0.73	0.72	0.58	0.22	0.37	0.51	0.71	-0.01	0.69	0.41	1				
SALIN	-0.45	-0.93	-0.91	-0.86	-0.68	-0.17	-0.24	-0.91	-0.31	-0.68	-0.21	-0.62	1			
TEMP	0.01	0.48	0.50	0.38	0.47	-0.42	-0.06	0.49	0.30	0.29	-0.38	0.21	-0.64	1		
HET. PICO	0.46	0.74	0.73	0.74	0.33	0.53	0.62	0.73	0.24	0.74	0.44	0.81	-0.72	0.23	1	
PHOT. PICO	0.11	0.35	0.39	0.43	0.10	0.04	0.25	0.39	0.37	0.55	0.28	0.35	-0.48	0.41	0.64	1

P<0.01, R ≥ 0.6310, df=12
P<0.05, R ≥ 0.5126, df=12

	N-NH4	N-NO2	N-NO3	SiO2	P-PO4	DOP	DON	DIN	APA	AMA	CHLa	OXY	SALIN	TEMP	HET. PICO	PHOT. PICO
N-NH4	1															
N-NO2	0.11	1														
N-NO3	-0.15	-0.37	1													
SiO2	-0.49	0.02	0.08	1												
P-PO4	0.02	-0.07	0.23	0.65	1											
DOP	0.58	0.06	-0.21	-0.70	-0.46	1										
DON	0.08	-0.08	-0.35	0.19	-0.02	-0.10	1									
DIN	0.63	-0.14	0.67	-0.29	0.20	0.26	-0.23	1								
APA	0.56	0.14	-0.23	-0.75	-0.36	0.76	0.00	0.23	1							
AMA	0.34	-0.14	-0.24	-0.55	-0.15	0.30	0.20	0.04	0.66	1						
CHLa	-0.41	0.05	0.01	0.21	0.04	-0.28	0.06	-0.30	0.10	0.29	1					
OXY	0.48	0.19	-0.25	-0.63	-0.15	0.44	-0.05	0.16	0.86	0.58	0.12	1				
SALIN	-0.38	0.21	-0.17	0.54	0.14	-0.36	0.04	-0.40	-0.16	-0.15	0.65	-0.17	1			
TEMP	0.09	-0.43	0.43	-0.19	0.06	0.05	0.00	0.39	-0.24	-0.12	-0.62	-0.21	-0.88	1		
HET. PICO	0.41	0.19	-0.12	-0.39	-0.21	0.02	0.24	0.23	0.43	0.43	0.04	0.53	-0.22	-0.03	1	
PHOT. PICO	-0.02	-0.07	-0.16	-0.19	-0.14	0.06	-0.05	-0.17	0.18	0.53	0.10	0.11	-0.03	-0.10	-0.10	1

P<0.01, R ≥ 0.6310, df=12
P<0.05, R ≥ 0.5126, df=12

Table 38

3.7. Discussion

Data elaboration by PCA on enzymatic activities monitored fortnightly from January 2004-October 2004 on station C1 reviled different patterns according to sampling depth on station C1 (Appendix). High significant correlation coefficients between phytoplankton, especially Bacillariophyceae, and APA were found on nearly all depths, making in evidence a condition of probable phosphorus deficiency on this station, where, due to very low phosphate concentrations, cells

are induced to synthesize APA in order to obtain P from the dissolved organic P-pool. Also positive correlation coefficients between APA and heterotrophic and phototrophic picoplankton were found, but on different depths. Heterotrophic picoplankton was the only biological parameter which correlated with APA on 15m (bottom), evidencing that also on this depth P-deficiency is present. Phototrophic picoplankton was positively correlated with APA, but only on 10m. The yearly variations of APA followed to some degree that of dissolved organic phosphorus (DOP). This could best be noticed by applying a moving average to the data, however high positive correlation coefficients (PCA) between APA and DOP were found on all depth, but 15m., while no significant correlations could be found between APA and particulate phosphorus (PP) or phosphate. The fact that no negative correlation between APA and inorganic phosphorus could be found during this survey could be do to the very low phosphate concentrations always found on the station, thus, cells were induced to synthesize APA because phosphorus deficiency was probably always present. Highly significant positive correlation coefficients between DOP and Bacillariophyceae were evidenced on all depth, while non correlation between DOP and salinity could be found, indicating the DOP content is not due to fresh water input, but to biological processes in the water column. The temporal variation in aminopeptidase activity (AMA) followed that of APA to some degree, with highest rates in late summers, and significant positive correlation coefficients between AMA and APA were found on all depths, but AMA did not correlate with any of the biological parameters considered. Regarding the different nitrogen fractions, only positive correlation coefficients between AMA and particulate nitrogen (PN) were found at 10 and 15m. Interestingly, positive correlation coefficients between PN and phytoplankton and phototrophic picoplankton were obtained at 5m., and on the same depth, high significant coefficients were found between DON and heterotrophic and phototrophic picoplankton, indicating that on this depth, biological processing of dissolved organic nutrients are highly active.

In order to obtain further information on the nutrient dynamics in the Gulf, daily sampling took place for one week in four meteorological seasons, starting in Spring (April 2006), ending in late Winter (March 2007) with intermediate samplings in Summer (July 2006) and Autumn (November 2006). The lowest APA and AMA rates were evidenced in Spring, which was also the period with lowest water temperature and salinity values. As in 2004, during the study on monthly variations (Cap. 3.3), the highest APA rates were evidenced in Summer, when phytoplankton Spring bloom have exausted the availability of DIN. Summer is also the period with the lowest Isonzo and Timavo discharged. The highest AMA rates were also recorded in Summer but only at the bottom. At the surface the highest AMA rates were detected in Autumn. Positive correlation coefficients were found between AMA and Chlorophyll *a* suggesting a strong role of phototrophs in the protein support stimulating the enzymatic degradative activity.

The elaboration of the data from samplings with different time frequencies revealed correlations which were not revealed during the classic monitoring approaches.

The most important result of this approach is the evidence of the information obtained with different

timing in the sampling strategy. A more frequent sampling put in evidence the relationships between nutrient consumers and remineralization processes and are preferable when the aim is to understand the ecological dynamic of the ecosystem.

4.1 Conclusions:

1) Isonzo River is a source of inorganic nutrients, and of Particulate Phosphorus, but not of DON and DOP, and the PO4 signal of river outflow does not reach the center of the Gulf.

2) In the Gulf, the dissolved organic pool of N and P is by far greater than the inorganic and particulate ones.

3) At station C1, no correlation between DOP and salinity could be evidenced suggesting that the Dissolved Organic Matter content is mainly due to processes of autochthonous origin. High positive correlation coefficients between DOP and phytoplankton biomass reinforces this hypothesis.

4) Data from stations nearest Trieste (A-transect) has not made in evidence any abnormalities regarding nutrients, contrary to was found in 1991 (sewage; high PO4)

5) Ecto-enzymatic activities can provide fundamental information for the understanding of complex nutrient dynamics of the system.

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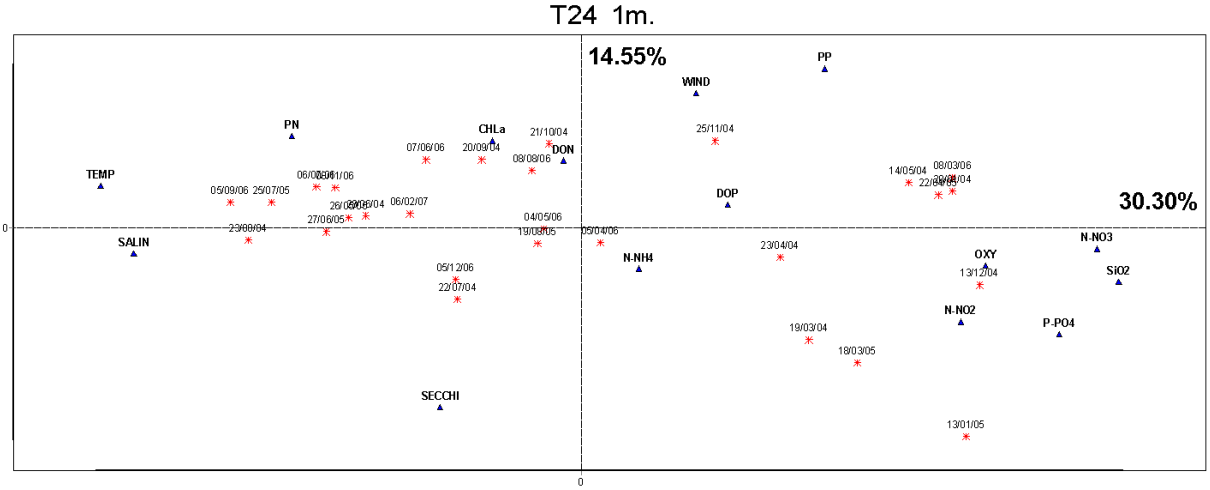
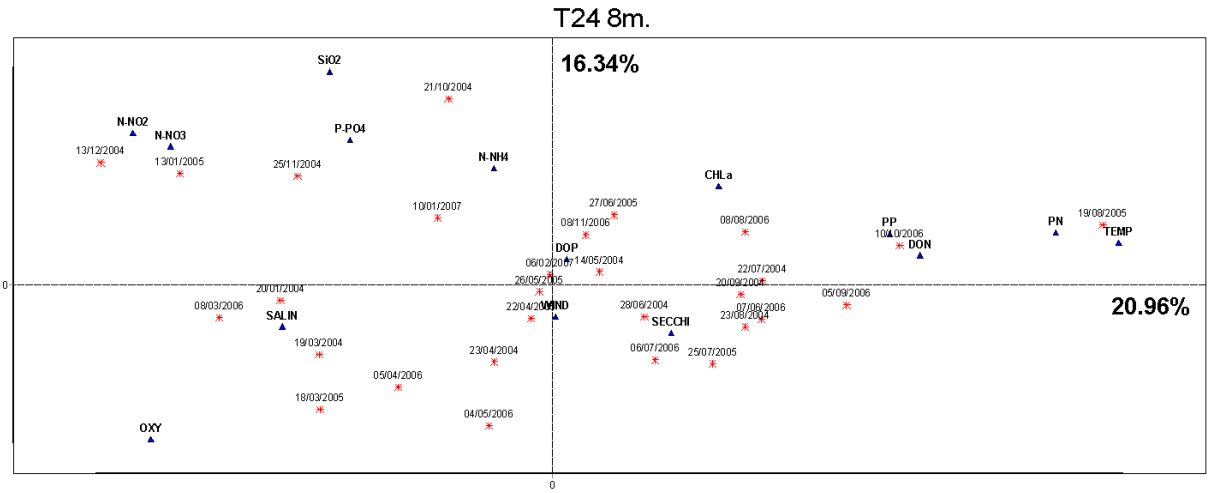
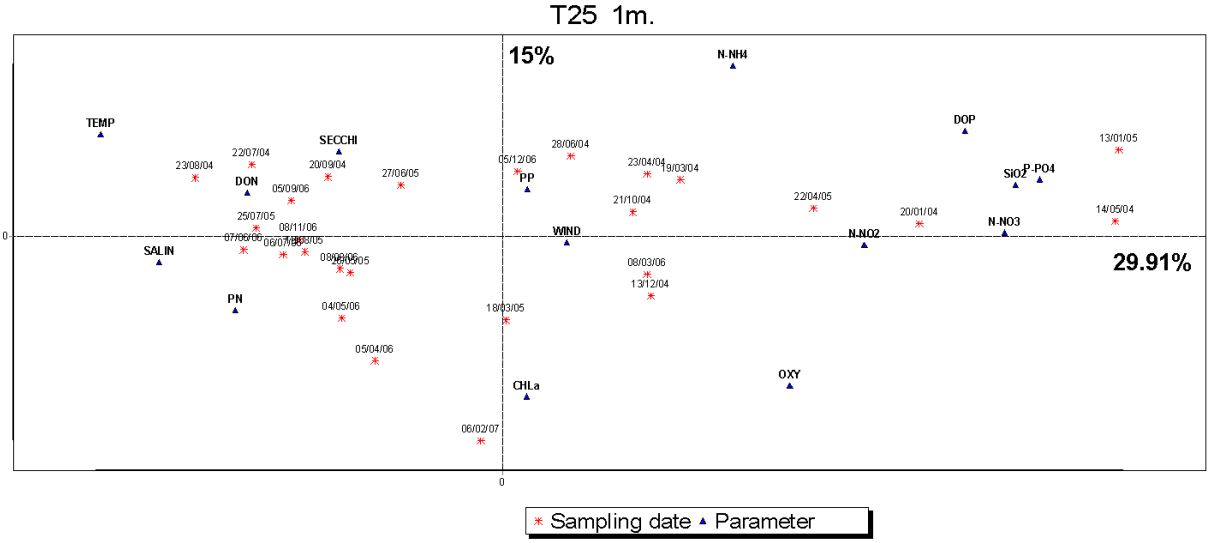
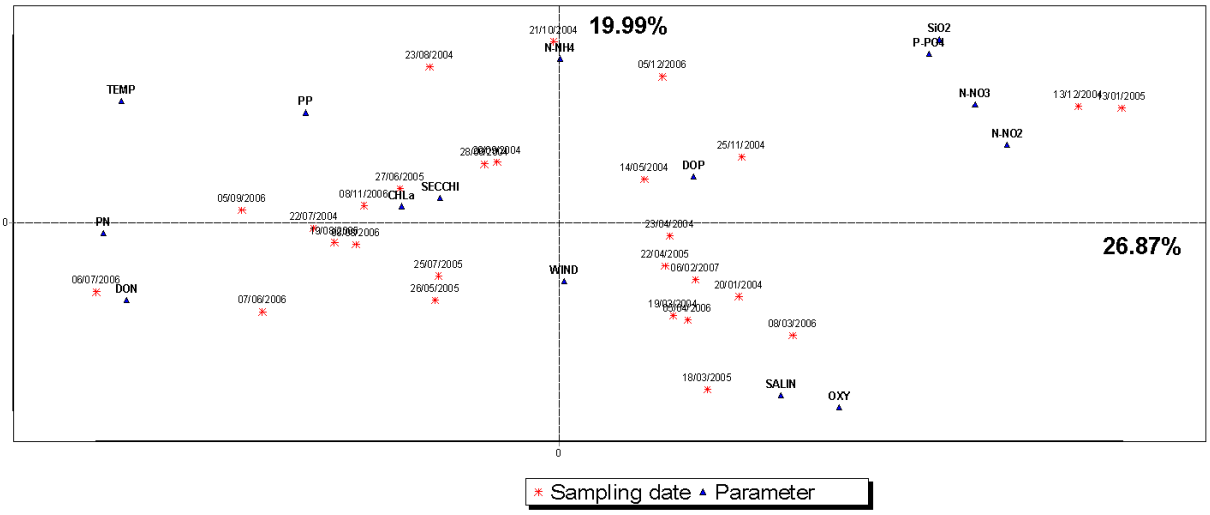
Appendix.


T24 1m.
14.55%
30.30%
PP
WIND
PN
CHLa
DON
TEMP
DOP
SALIN
N-NH4
N-NO3
OXY
SiO2
N-NO2
P-PO4
SECCHI
Sampling date
Parameter

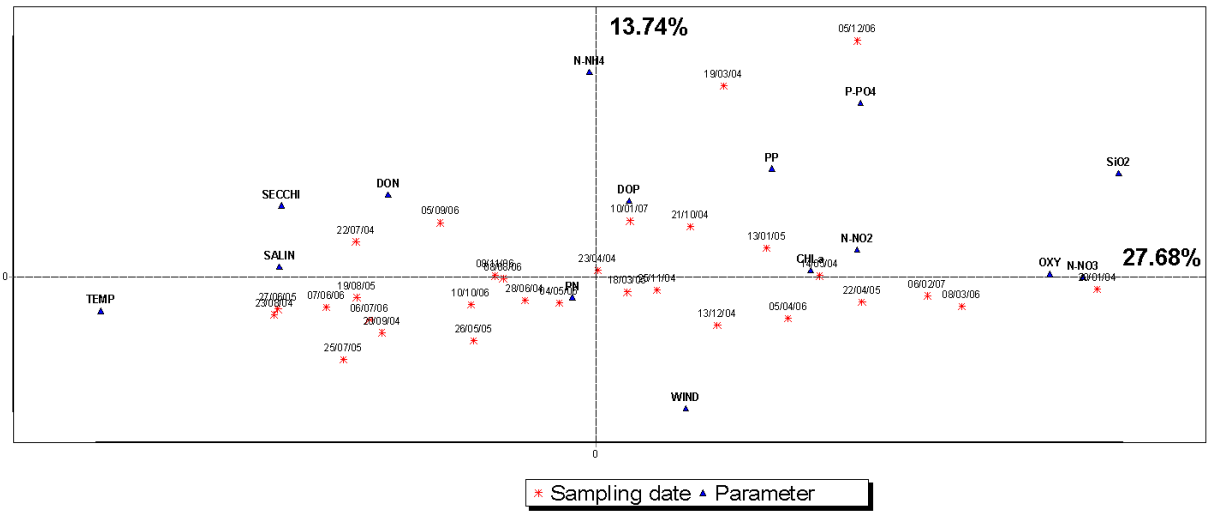

T24 8m.
16.34%
20.96%
SiO2
N-NO2
N-NO3
P-PO4
N-NH4
CHLa
PP
PN
TEMP
DON
DOP
WIND
SECCHI
SALIN
OXY
Sampling date
Parameter


T25 1m.
15%
29.91%
N-NH4
TEMP
DOP
SECCHI
PP
DON
SALIN
WIND
N-NO2
N-NO3
SiO2
P-PO4
PN
CHLa
OXY
Sampling date
Parameter

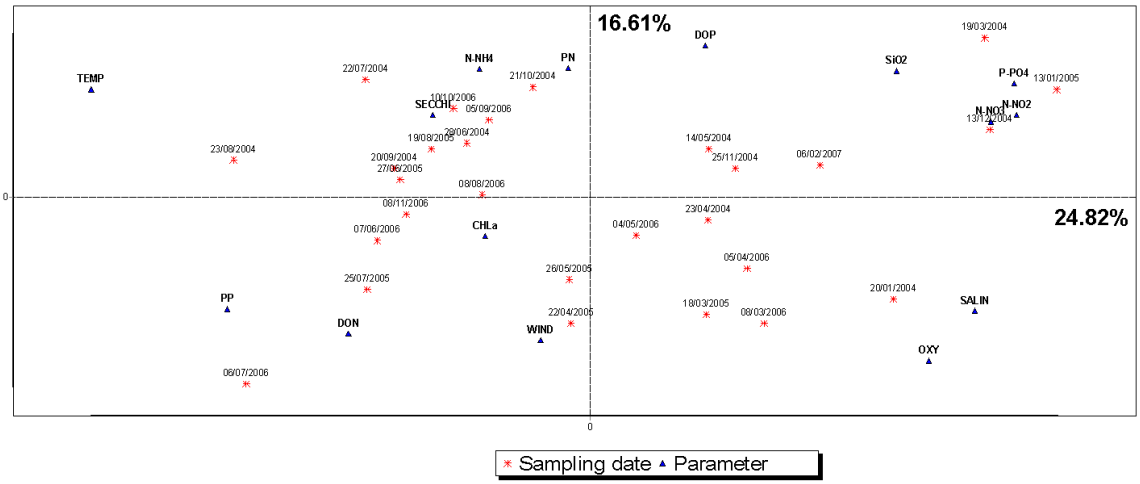
T25 11m.



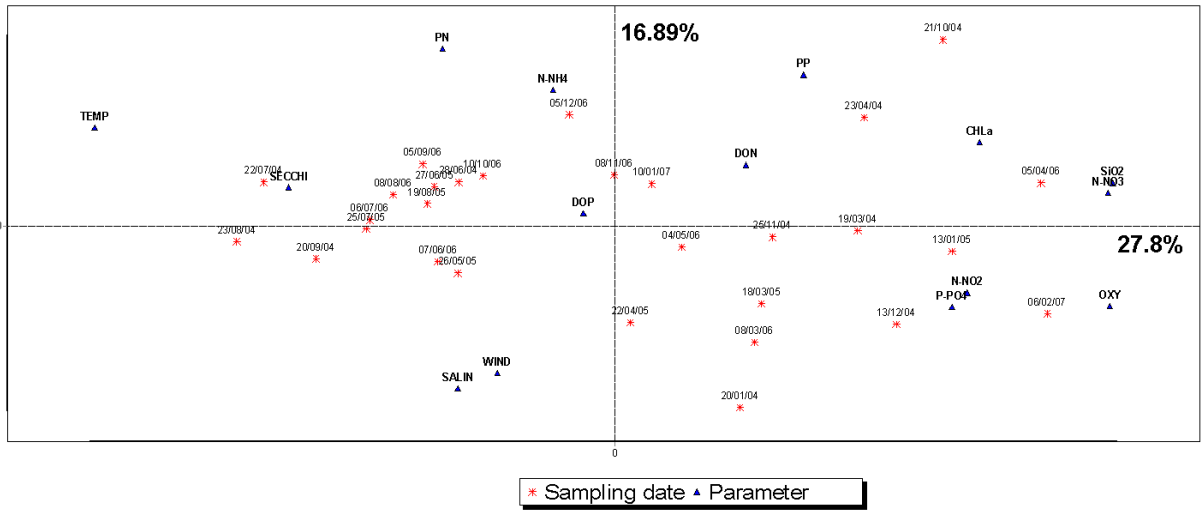
T03 1m.



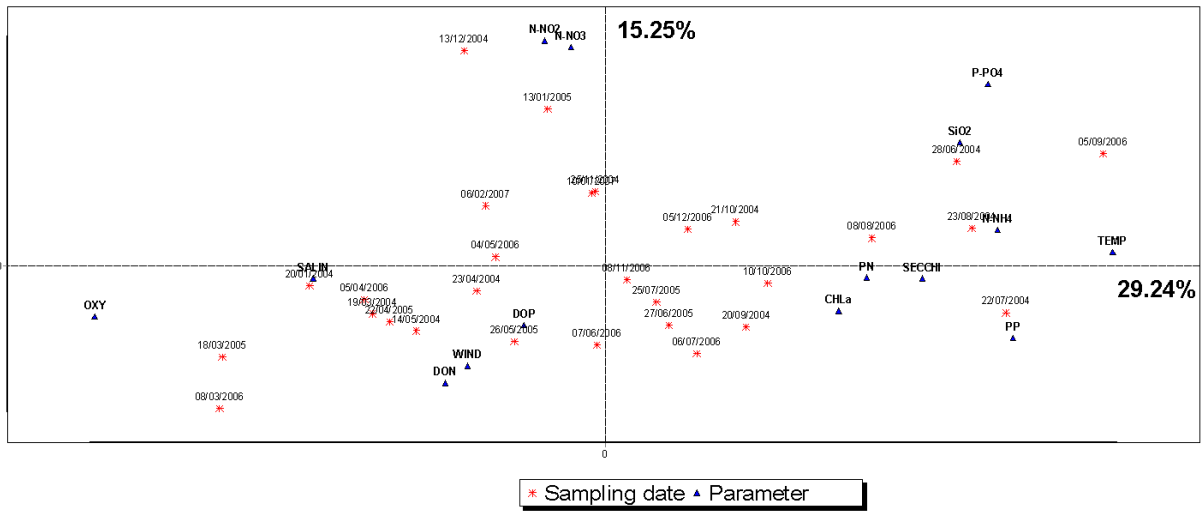
T03 14m.



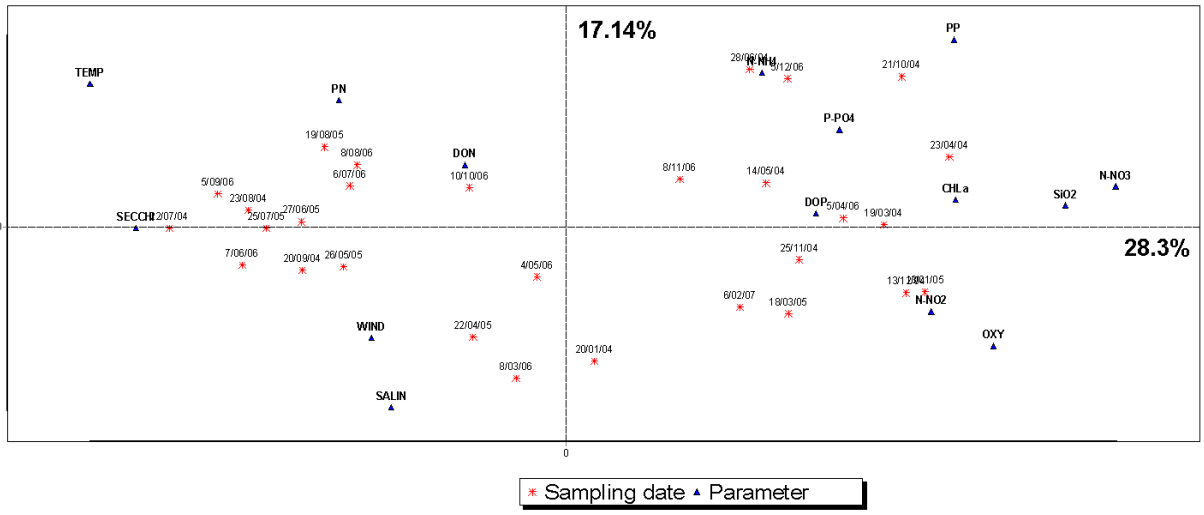
T08 1m.



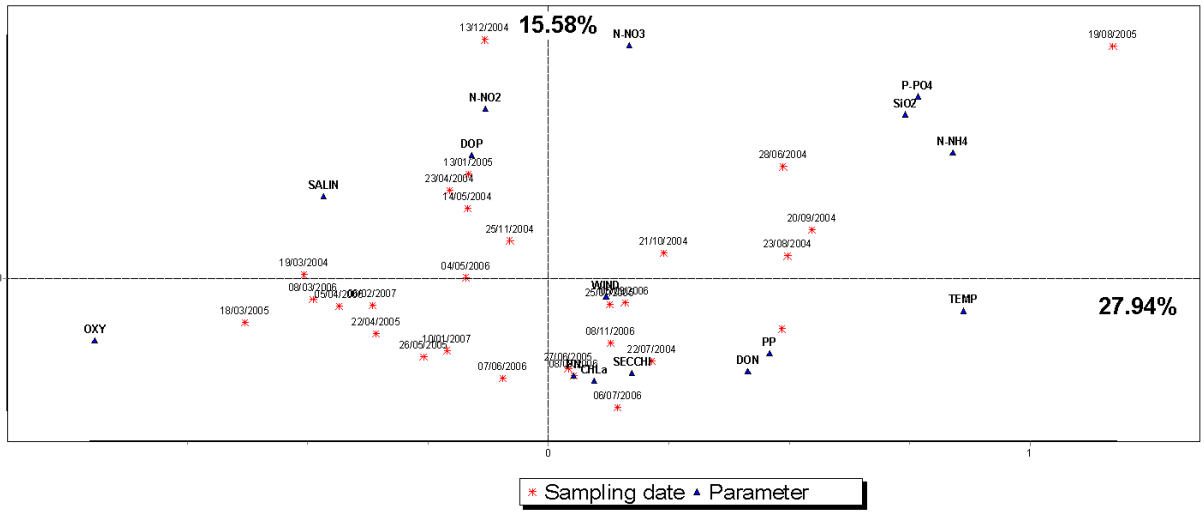
T08 23m.



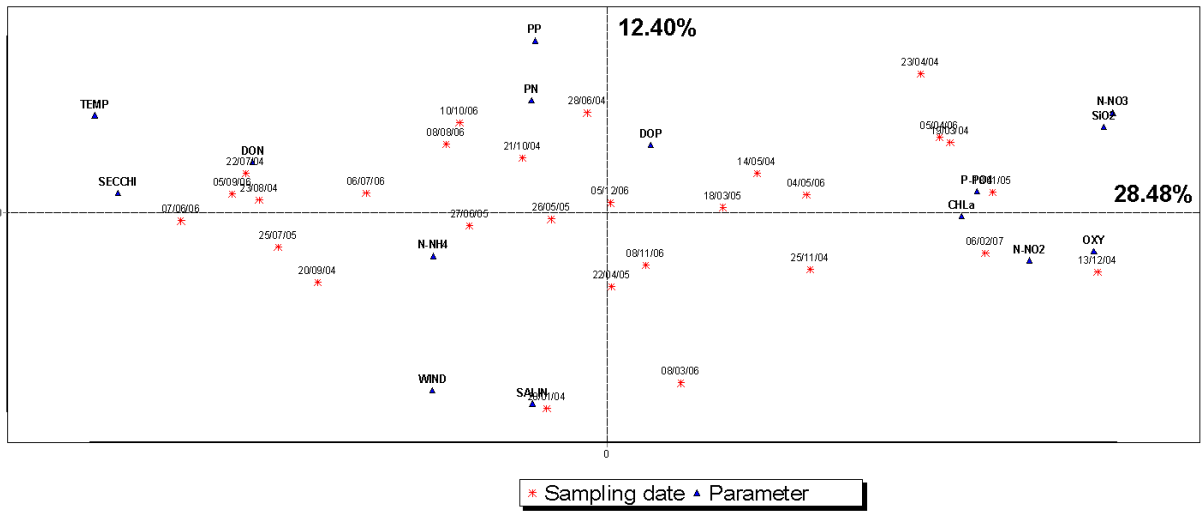
T26 1m.



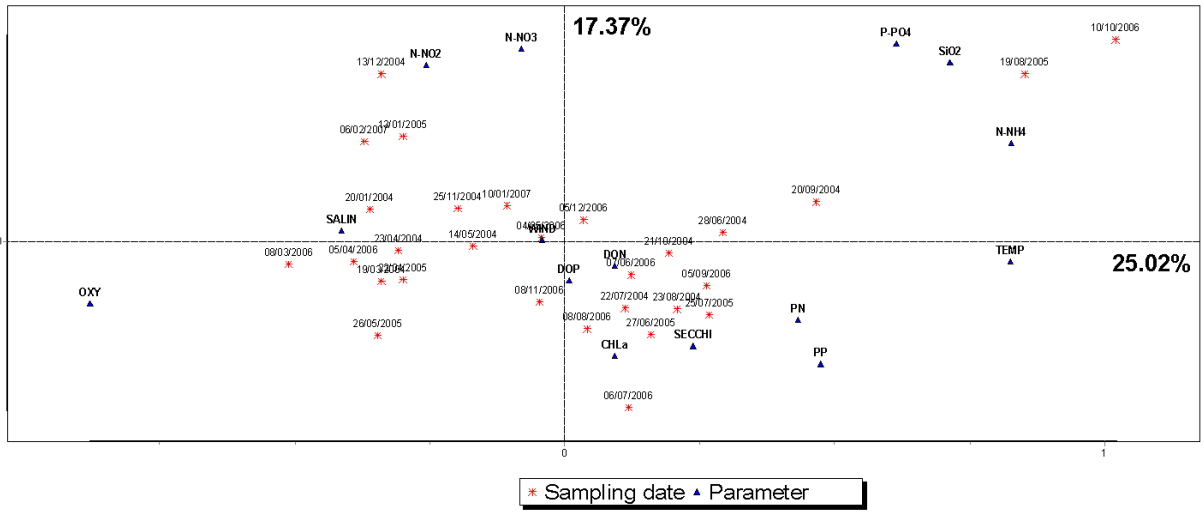
T26 23m.



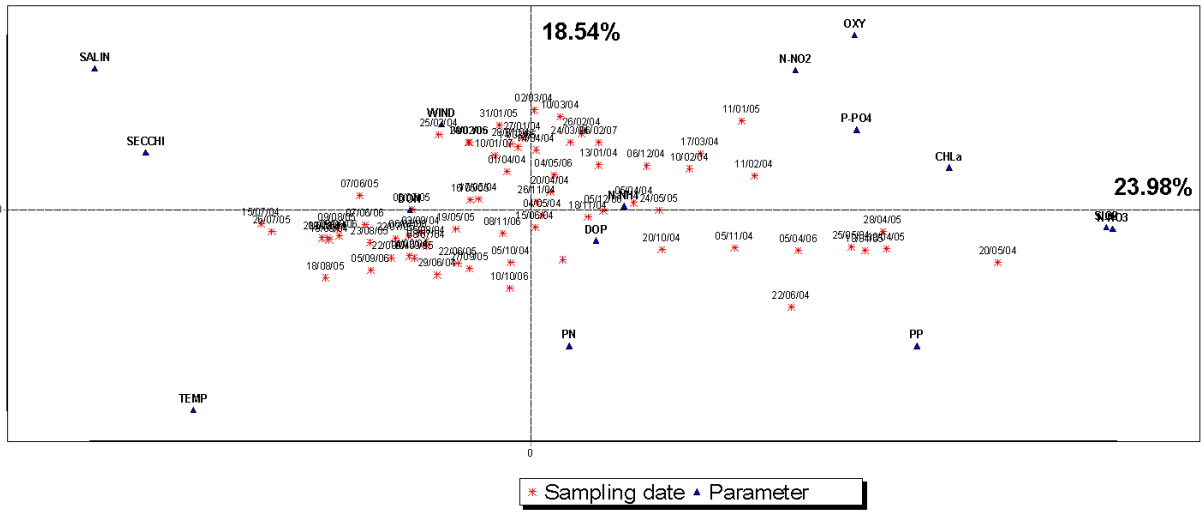
T11 1m.



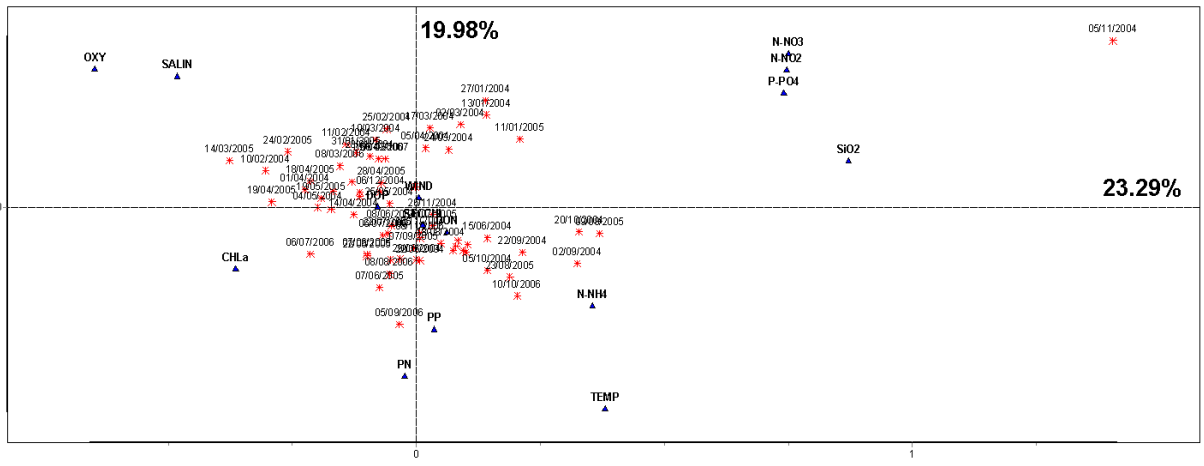
T11 23m.



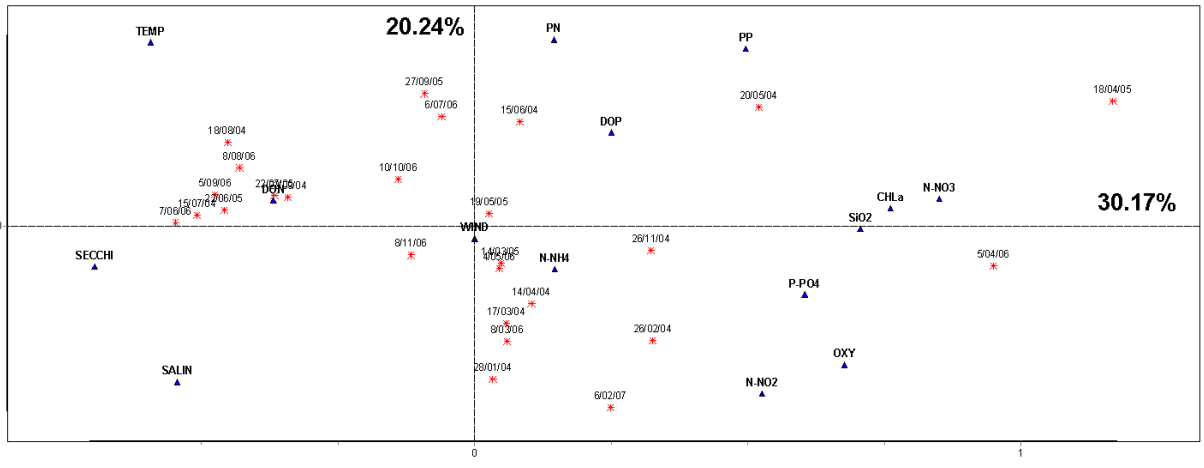
C1 1m.



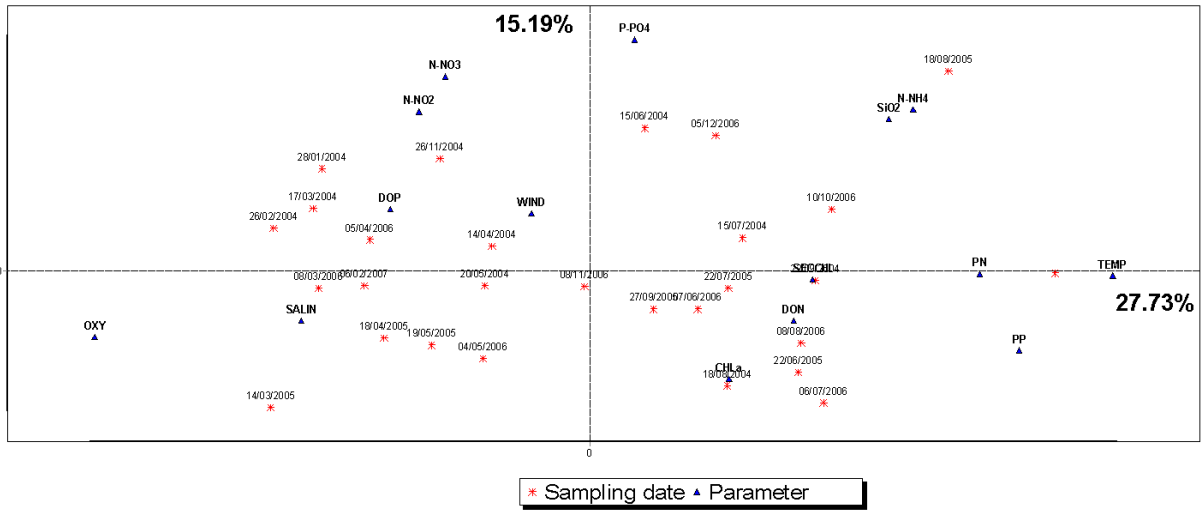
C1 15m.



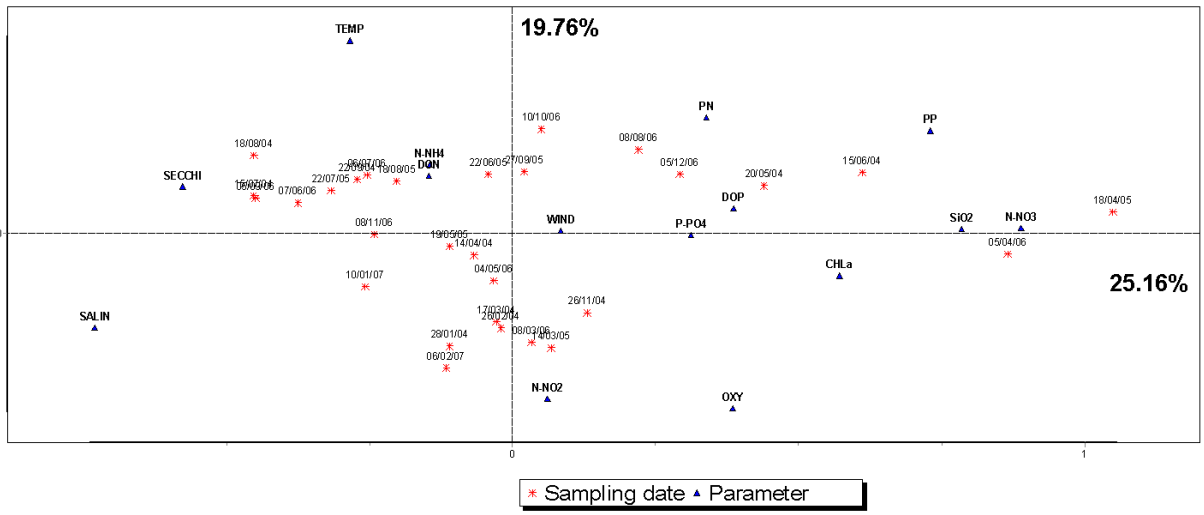
T22 1m.



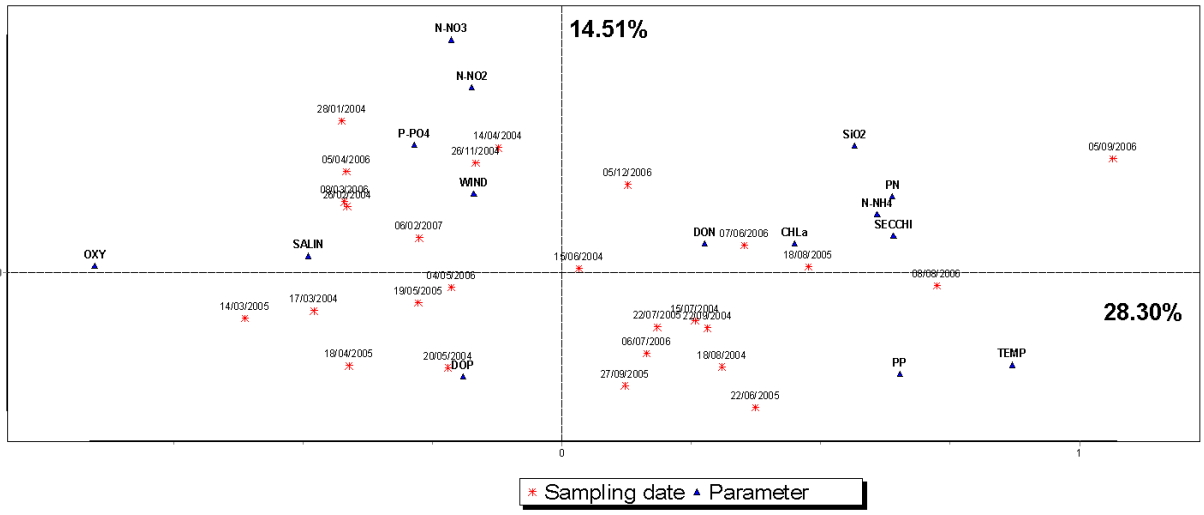
T22 18m.



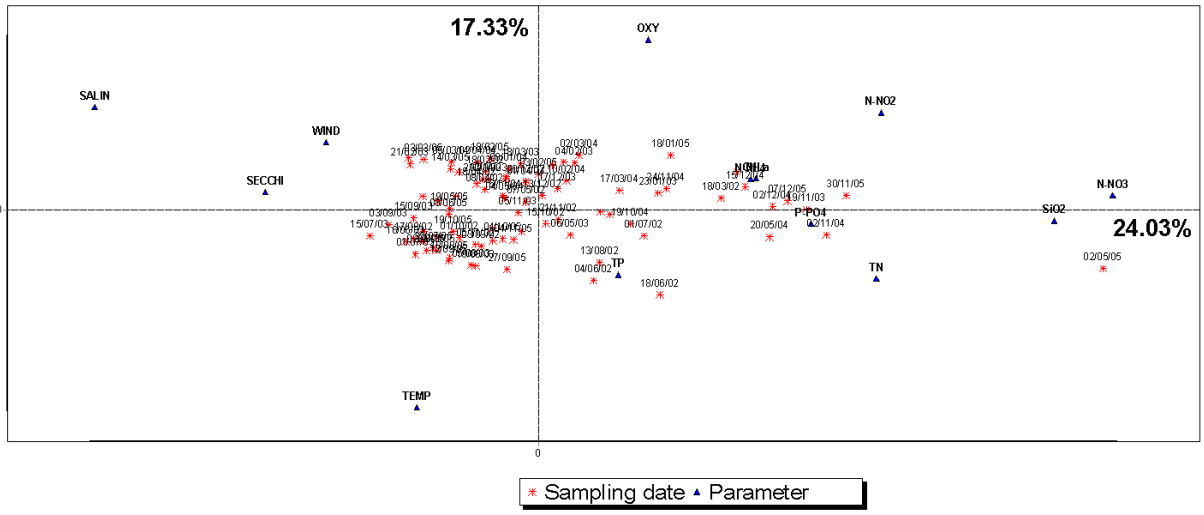
T23 1m.



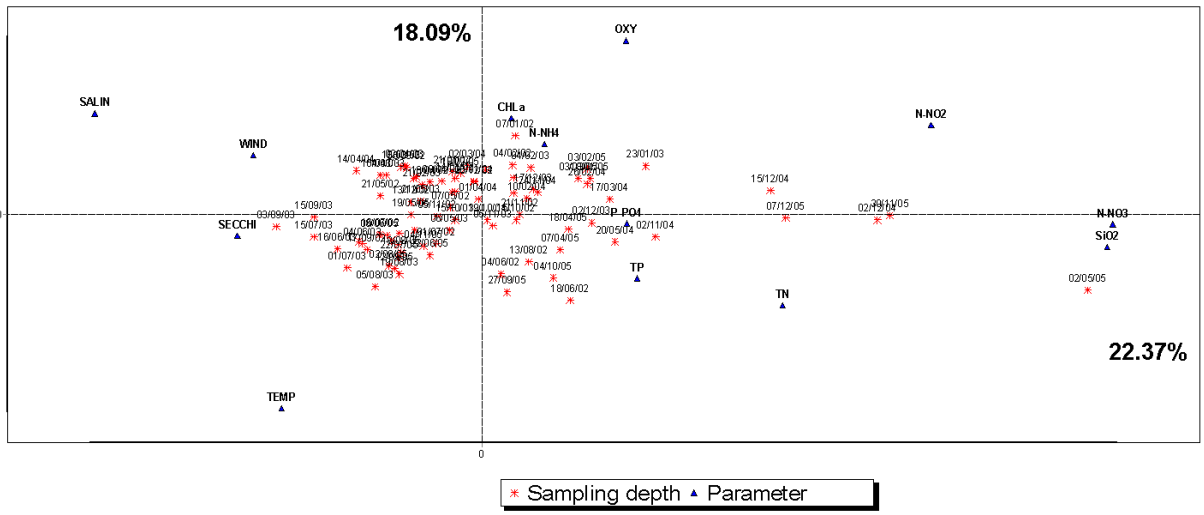
T23 18m.



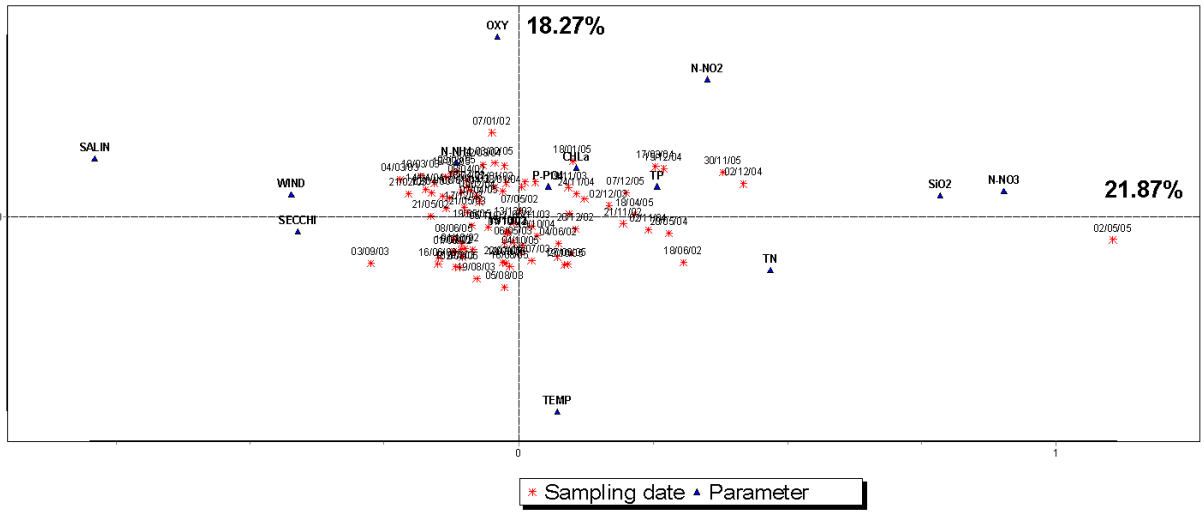
A0 1m.



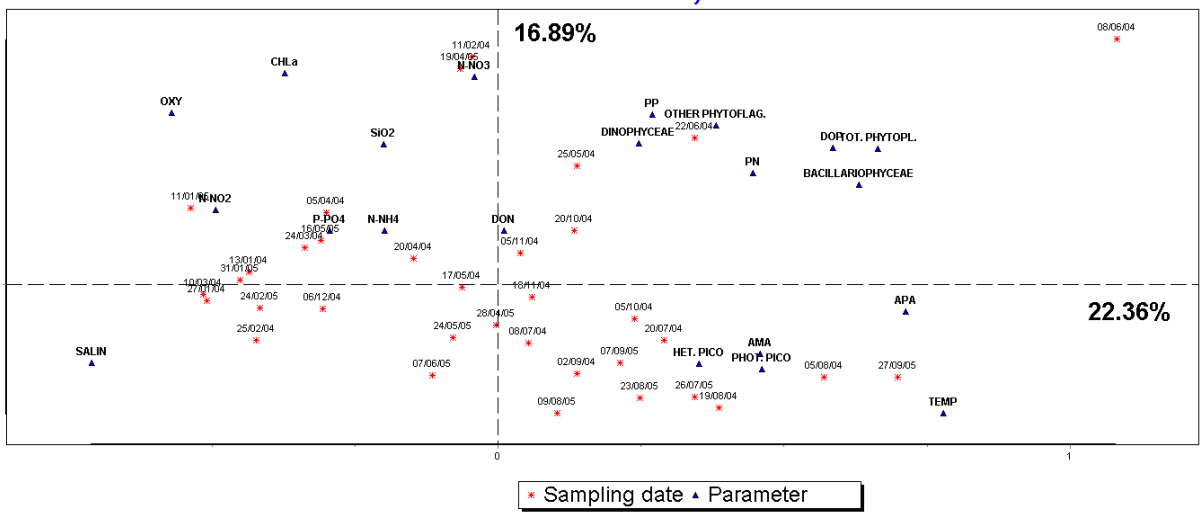
A2 1m



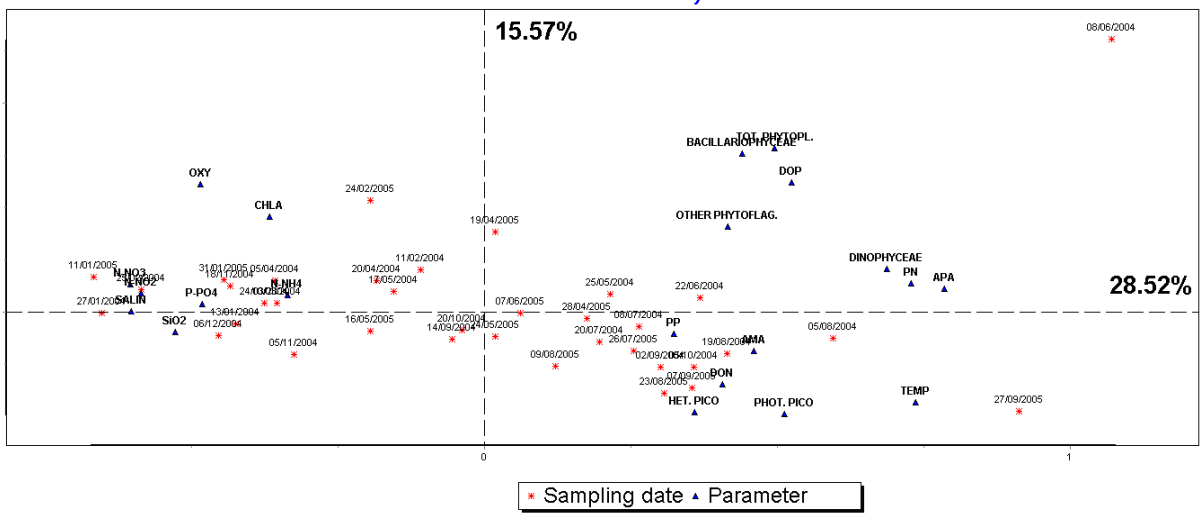
A3 1m.



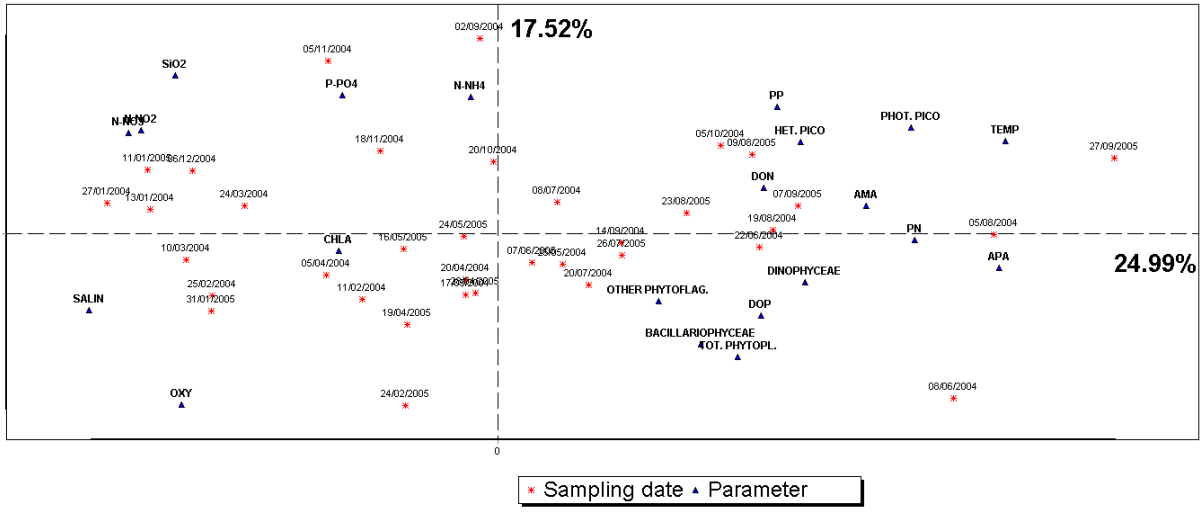
C1 1m. Annual and monthly variations



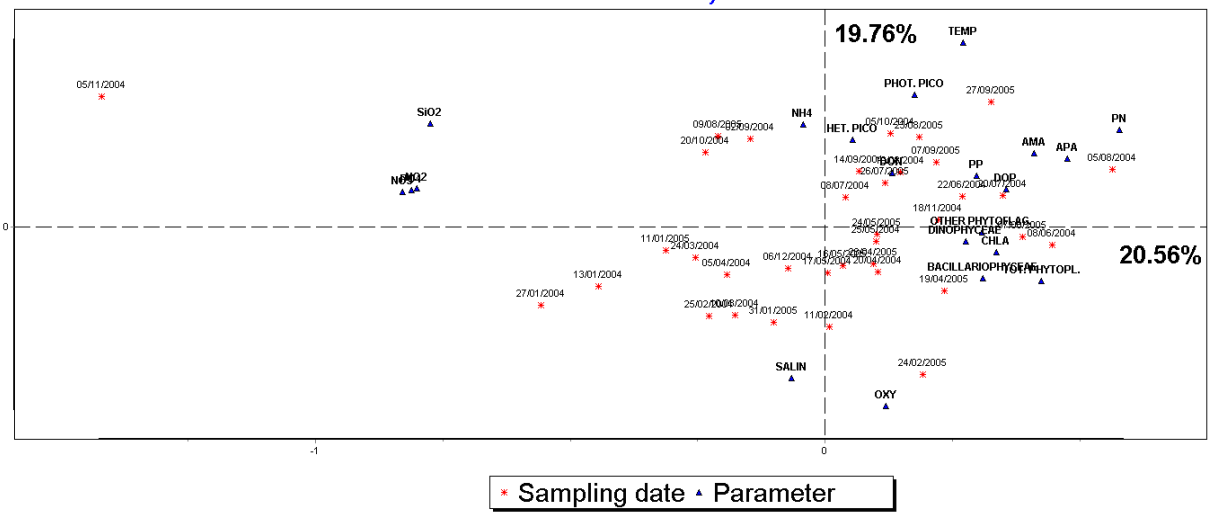
C1 5m. Annual and monthly variations



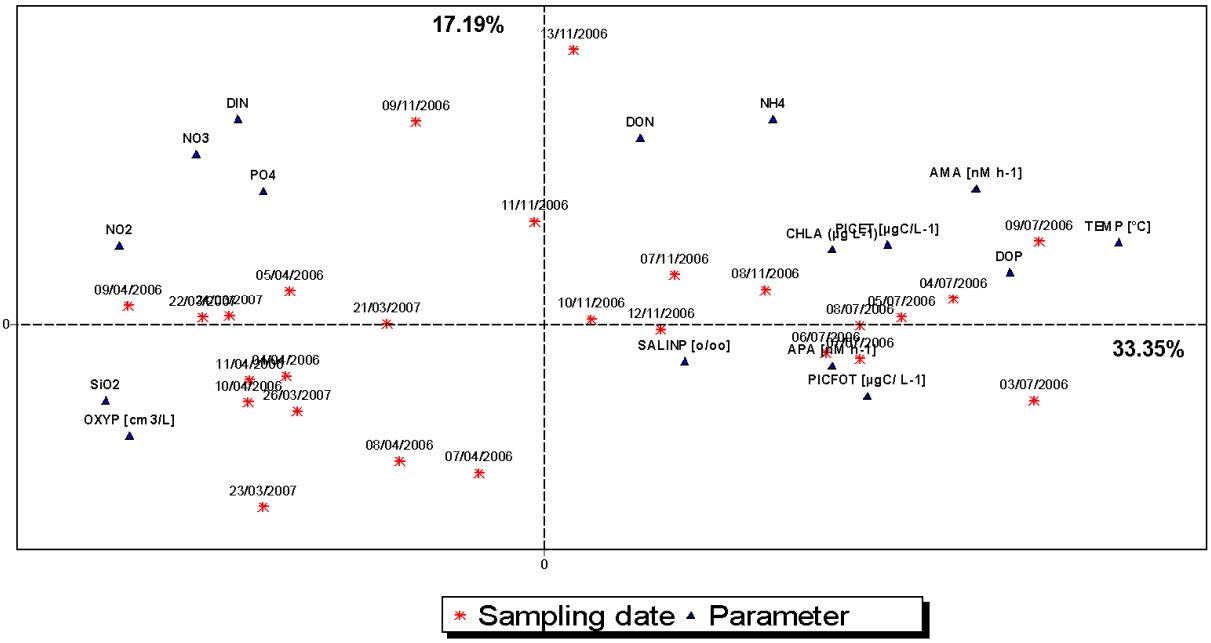
C1 10m. Annual and monthly variations



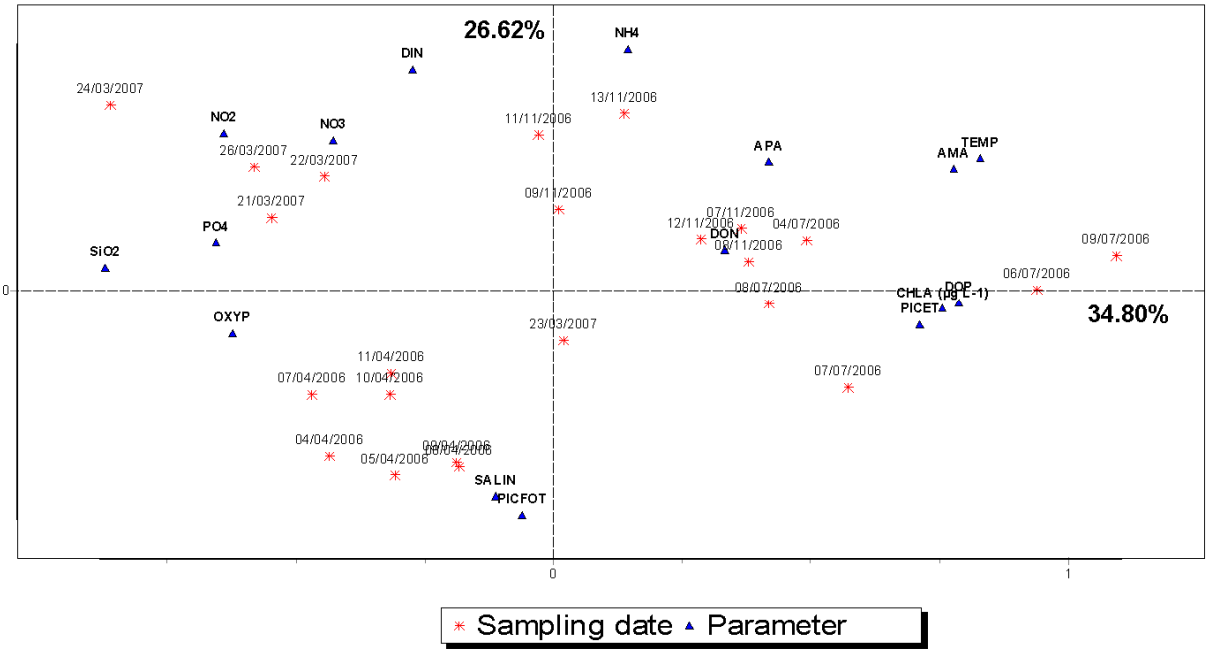
C1 15m. Annual and monthly variations

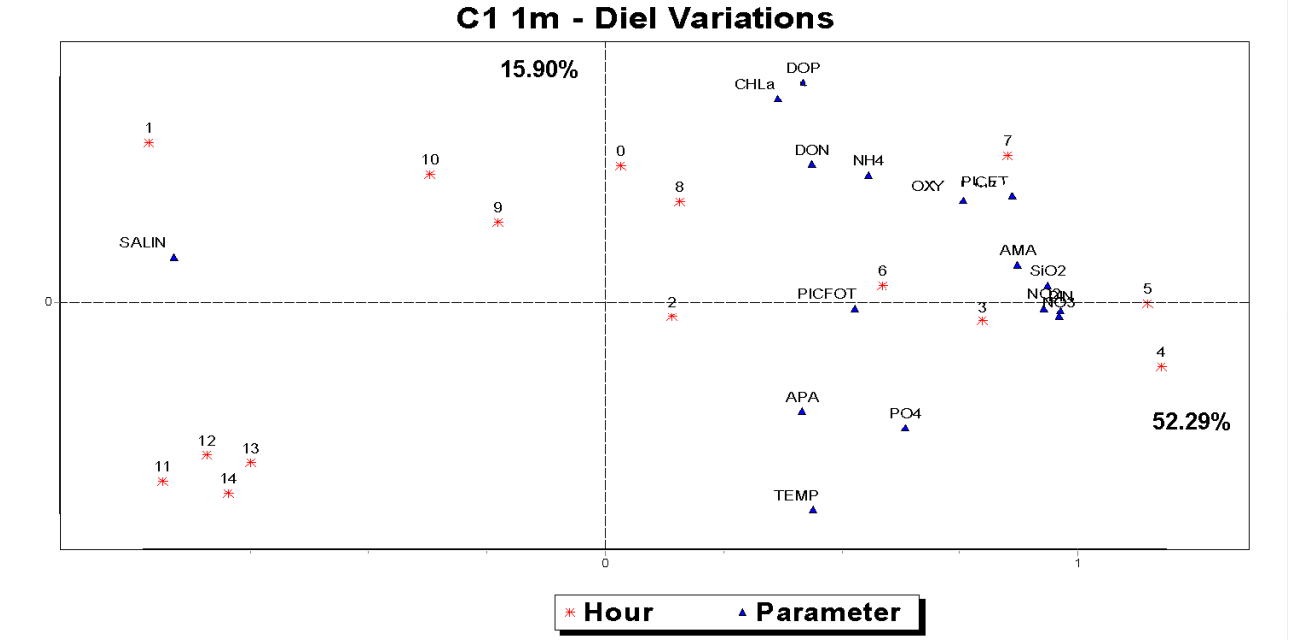


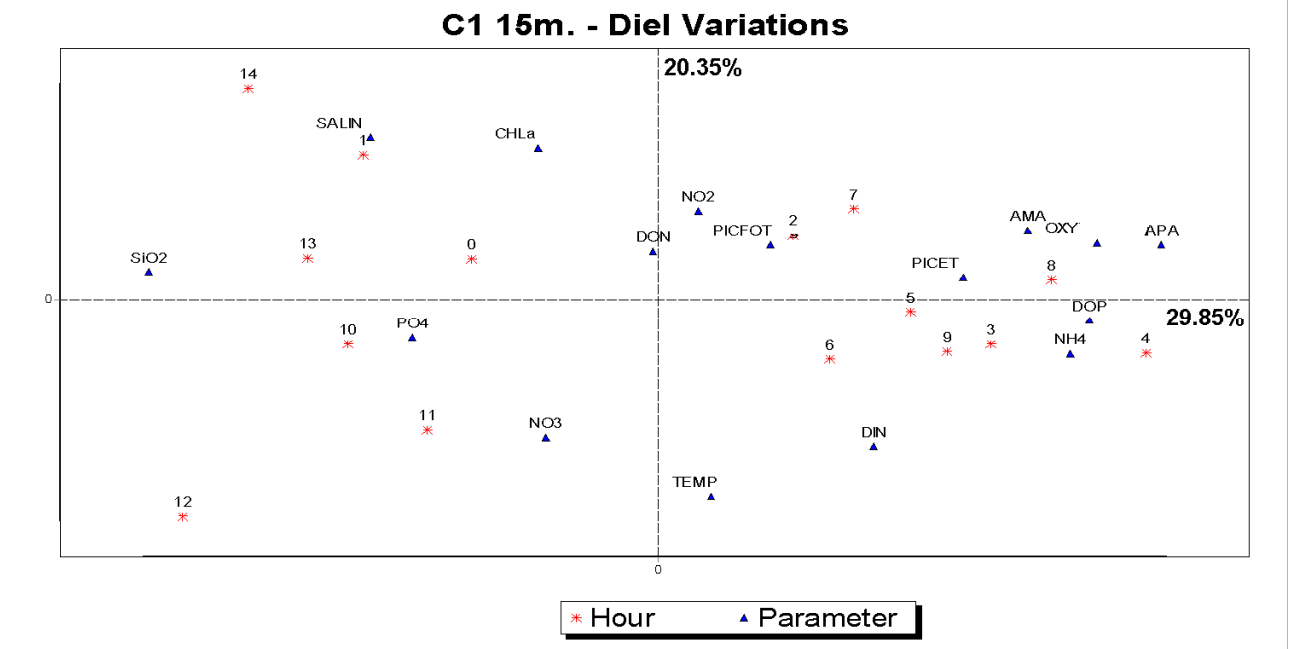
C1 - 1m - Seasonal Variations



C1 - 15m - Seasonal Variations




C1 1m - Diel Variations
15.90%
52.29%
DOP
CHLa
DON
NH4
OXY
PICET
AMA
SiO2
NO2
NO3
PICFOT
APA
PO4
TEMP
SALIN
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Hour
Parameter


C1 15m. - Diel Variations
20.35%
29.85%
SALIN
CHLa
NO2
PICFOT
DON
AMA
OXY
APA
PICET
SiO2
PO4
DOP
NH4
NO3
DIN
TEMP
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Hour
Parameter