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**BIOGEOCHEMICAL PROCESSES AND NUTRIENT CYCLING WITHIN AN
ARTIFICIAL REEF OFF SOUTHERN PORTUGAL**

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ABSTRACT

This study (2002/2004) examines the effect of artificial reef (AR) structures off the southern coast of Portugal on biogeochemical process and nutrient cycling. Organic and inorganic carbon, nitrogen, phosphorus and chlorophyll *a* were determined monthly in sediment cores and settled particles for a two-year period. Ammonium, nitrates, phosphates, silicates, total organic nitrogen and phosphorus, chlorophyll *a* and phaeopigments were also determined monthly in water samples within AR and control sites. Results of the two-year study showed that: i) there was a significant exponential fit between organic carbon and chlorophyll *a* ($r^2=0.91$; $p<0.01$) in reef sediment suggesting an increase of benthic productivity; ii) organic carbon and nitrogen content in settled particles within AR environment was about four times higher two years after reef

deployment; iii) nutrients and chlorophyll *a* in the water column were higher at AR than control site. Two years after AR deployment, dissolved organic and inorganic compounds in near bottom water were 30 to 60 % higher, emphasizing benthic remineralization processes at AR's organically rich sediment. Marked chemical changes in the ecosystem were observed during the two-year study period, reinforcing the importance of these structures for sandy coastal areas rehabilitation through trophic chain pull-out.

KEY WORDS: artificial reefs, benthic remineralization, biogeochemical process, nutrients, temporal changes.

INTRODUCTION

In recent years, great strides have been made in the understanding of artificial habitat ecology, although many questions regarding their performance and environmental impacts remain unanswered (Carr & Hixon, 1997). One of the reasons for the poor understanding of AR ecology is the lack of knowledge of their effect on the surrounding natural environment (Sheng, 2000; Svane & Petersen, 2001), which is a fairly new area of AR research. Scientific literature in this field is scarce and commercial technological applications have not been developed (Antsulevich, 1994). In Portugal, research regarding these systems has been mainly focused on ichthyological fauna, especially on commercial species (Santos & Monteiro, 1997, 1998; Santos et al., 2002, 2005) and benthic communities (Boaventura et al., 2006; Moura et al., 2004, 2006).

Reef structures, by providing protection for marine species, can result in marine system biomass enhancement (Santos & Monteiro, 1997, 1998; Godoy et al., 2002) with

associated changes in local productivity (Grossman et al., 1997; Pickering & Whitmarsh, 1997). As a result of biomass enhancement sediment becomes more active in the process of nutrient regeneration providing a nutritional source for other forms within the ecosystem (Rizzo, 1990), or being exported by water movements increasing the general productivity of neighbouring areas. Furthermore, planktivorous fish species can induce nutrient production in the water column, excreting substantial amounts of ammonium, urea and depositing organic material, which is then incorporated into the reef food web. This process implies the increase of productivity and diversity on a local scale by increasing biotic and abiotic habitat complexity (Ambrose & Anderson, 1990), promoting biological colonization and species richness in many ecological niches and food webs (Relini et al., 1994).

In productive ecosystems the biogeochemical processes are extremely complex due to the interactions with the sediments and the benthic-pelagic competition of primary producers (Fourqurean et al., 1993). In the case of nitrogen, sediments are a source as well as a major sink in the cycling of this element regulating its concentration and thus, the productivity of coastal marine systems (Lohse et al., 1993). Phosphorus is an essential nutrient for the growth of marine phytoplankton and has been suggested as the limiting factor for ocean primary production (Howarth et al., 1995). Most of P-removal from the water column takes place through sedimentation of organic matter (Berner et al., 1993). Consequently, it is of prime importance to know the fate of the phosphorus in organic matter upon reaching the sediment (Slomp, 1997).

In the present study a survey was carried out during a two-year period in order to better understand AR's biogeochemical processes, the chemical composition of settled

particles and nutrient cycling. The main goal of this study was to evaluate the trophic chain pull-out promoted by the deployment of concrete blocks on a sandy coastal area through organic matter deposition, benthic remineralization and local productivity.

METODOLOGY

Study site

The location of the study area was approximately 2.5-4.0 km off Faro (Algarve, Southern Portugal) on a flat sandy bottom (Figure 1). These sediments range from coarse sand (500 μm) to fine sand (125 μm). Drift currents tend to run along the shore, to depths of 30 m or more (Moita, 1986; Melo, 1989). The current speed may in extreme conditions reach 0.5 m s^{-1} . Tides are semi-diurnal with a mean tidal range of 2 m, with a maximum of 3.5 m and a minimum of 0.5 m. The Faro/Ancão AR consists of 5.460 concrete cubic units (2.7 m^3 each), distributed in 52 reef groups, occupying a narrow strip (6.727 ha), at depths ranging from 17 to 25 m (shallow waters). A sediment-trap with 6 PVC tubes (5 cm diameter and 50 cm length) was placed on a random reef block group (A₁₀) immediately after its deployment (August 2002).

Field sampling

Water sampling was carried out at **AR** group A₁₀ (37° 01' N; 7° 55' W) and at a control site-C (37° 01' N; 7° 57' W) located about 1.5 km from the AR (Figure 1) to eliminate or minimize the possibility that it might be affected by the presence of the man-made blocks. A multi-parameter deep-sea probe (Yellow Spring-mod.YSI 6820) was deployed *in situ* to determine temperature, dissolved oxygen and pH. Water samples were collected down the water column (surface-0.5 m; mean depth-10 m; and bottom-20 m: three replicates at each depth), using a Niskin bottle, during the years 2003 and 2004

(February, May, August and November). Samples were stored in leakproof polycarbonate vials, completely filled and kept in a refrigerated chamber prior to determining ammonium, nitrate, phosphate, silicate, organic nitrogen and phosphorus, chlorophyll *a* and phaeopigments. Sediment-trap tubes were collected and replaced each month by divers during Summer 2002 (August and September); Autumn 2002/Winter 2003 (October, November, December, January and February); Spring/Summer 2003 (April, May, July and August); Autumn 2003/Winter 2004 (September, October, December, January, February) and Spring/Summer 2004 (March, July, August and September). Organic and inorganic carbon, nitrogen and phosphorus were determined in settled particles. Divers simultaneously collected ten random sediment cores within the reef group (monthly from August 2002 to September 2004). Samples were kept in a refrigerator chamber prior to determining organic and inorganic carbon, nitrogen and phosphorus, chlorophyll *a* and phaeopigments.

Laboratory analysis

Solid fraction. Settled particles and sediment cores from upper layers (0-1 cm and 1-2 cm) were dried to 80°C until a constant weight and ground to a fine powder. Total organic carbon (TOC), nitrogen (TON) and phosphorus (TOP) were determined in the powder samples. Total organic (TOC) and inorganic carbon (TIC) and total inorganic nitrogen (TIN), were determined by a CNH analyser “NC 2500 CE instruments” using acetanilide as reference material (Byers et al., 1978). Total organic phosphorus was determined by digestion with HCl during 20 minutes at 200°C according to Andersen (1976). Phosphorus sorbed to lithogenic particles was sequentially extracted: phosphorus weakly bound (weakly bound-P), 1 hour stirring with NH₄Cl; phosphorus bound to calcium (Ca-bound P), 1 hour stirring with HCl and phosphorus bound to iron (Fe-bound

P), 17 hours stirring with NaOH according to Chang & Jackson (1957) and Hosomi & Sudo (1982). Chlorophyll *a* (Chl *a*) was extracted with acetone (90 %) from the upper sediment layers and determined by spectrophotometry according to Lorenzen (1967).

Water column. Water samples were filtered through 0.45 µm Millipore filters and stored at -4° C until nutrient analysis. Ammonium (NH₄⁺), nitrate (NO₃⁻), phosphate (HPO₄²⁻) and silicate Si(OH)₄ were determined using a “Skalar” autoanalyser (Skalar methodology). Detection limit used in the present method was 0.2 µM for ammonium and silicate and 0.05 µM for nitrate and phosphate. Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were analysed by potassium peroxodisulphate (K₂S₂O₈) oxidation in autoclave (1.5 bar; 120° C) as described in Grasshoff (1983) and oxidized forms determined in the autoanalyser. Chlorophyll *a* (Chl *a*) and phaeopigments (Phaeop) retained in filters were determined using a spectrophotometer “Hitachi 150-12” according to Lorenzen (1967).

Data analysis

Multivariate analysis of all information concerning water samples and its variability (Euclidian distance) was applied using Principal Component Analysis (PCA - Legendre & Legendre, 1984) involving the BRODGAR package “Software for Univariate & Multivariate Analysis and Multivariate Time Series” (Version 2.4.1). One-factor analysis of variance (ANOVA) was performed to test statistically significant differences between the upper sediment layers for TOC and Chl *a*.

RESULTS

Temporal changes in sediment composition: C, N, P and Chl *a*

Results of sediment characteristics from August 2002 (AR deployment date) to September 2004 are shown in Table 1. Two years after the reefs' deployment TOC, Fe-bound P and Chl *a* were respectively 100, 3 and 2 fold higher than those obtained immediately before the AR deployment. Over the studied period, TOC and Chl *a* concentrations were significantly higher in sub-layer (ANOVA; $n = 26$; $p < 0.01$), pointing to a hydrodynamic disturbance on the topmost sediment layer. During the studied period, organic nitrogen concentration in the seabed remained below the detection limit ($< 0.005 \mu\text{mol g}^{-1}_{\text{dw}}$), while TOP concentrations ($1.2 - 2.6 \mu\text{mol g}^{-1}_{\text{dw}}$) and sediment porosity ($0.28 - 0.31$) presented slight differences. A well-defined seasonal variation was exhibited by TOC, TIC, Fe-bound P and Chl *a*, reaching the highest concentrations in the sub-layer, during 2004 Spring/Summer period.

Temporal changes in composition of sediment-trap settled particles: C, N, P

The time course of changes in particulate organic carbon (POC), nitrogen (PON) and phosphorus (POP) content of settled particles within the AR is presented in Table 2. Results show a well-defined POC increased during the period of study. Mean concentrations of $590 \mu\text{mol g}^{-1}_{\text{dw}}$ were observed before AR deployment, reaching $2.330 \mu\text{mol g}^{-1}_{\text{dw}}$ and $3.292 \mu\text{mol g}^{-1}_{\text{dw}}$ during 2003 and 2004 Spring/Summer periods, respectively. PON concentrations followed the same temporal pattern. A mean PON value of $2.5 \mu\text{mol g}^{-1}_{\text{dw}}$ was found immediately before AR deployment, reaching $241 \mu\text{mol g}^{-1}_{\text{dw}}$ and $178 \mu\text{mol g}^{-1}_{\text{dw}}$ during the 2003 and 2004 Spring/Summer periods, respectively. Results also emphasize that POP mean concentration obtained before AR deployment ($6 \mu\text{mol g}^{-1}_{\text{dw}}$) reached values 1.5 to 2-fold higher during 2003 and 2004

Spring/Summer periods. Alongside the time series, biogenic compounds also exhibited a clear seasonal pattern, reaching maximum concentrations during the warmer periods.

C/N and N/P ratios – Before AR deployment the C/N ratio of settled particles was abnormally high, due to low PON concentrations (Figure 2). Six months after AR deployment, C/N ratio became close to Redfield value, remaining approximately constant over 2003 and 2004. An abnormally low N/P ratio (<2) was obtained before AR submersion resulting from the extremely low PON values. During 2003 and 2004 Spring/Summer periods, N/P ratio (Figure 3) reached standard values of 10 to 20.

Water column: spatio-temporal variability

Data on physical (Temp, DO and pH), chemical (NH_4^+ , NO_3^- , HPO_4^{2-} , $\text{Si}(\text{OH})_4$, DON, DOP) and biological (Chl *a* and Phaeop) parameters occurring in the water column, within the AR (**A**₁₀: R₀, R₁₀, R₂₀) and at the control site (**C**: C₀, C₁₀, C₂₀), were obtained during this study. Principal component analysis (PCA), applied to the overall data showed a spatial variability through a two-dimensional space, defined by two principal coordinate axes (A1 and A2). More than 50 % of the analysis is explained by the axis inertia. The descriptors (parameters) and location - A₁₀ (0.5 m; 10m; 20m) and C (0.5 m; 10 m; 20m) - at February, May, August and November of 2003 and 2004, are represented in the PCA (Figures 4_(a,b), 5_(a,b), 6_(a,b), 7_(a,b)).

February: spatial variability - AR near bottom water samples were closely associated with HPO_4^{2-} , DOP; NH_4^+ , DON, Chl *a* and Phaeop which have the highest contribution in negative axis 1 and 2 (Figure 4a). An opposite cluster was defined by the control site euphotic and bottom water samples, corresponding to the lowest nutrient concentrations.

Down the water column profile, the high similarity observed among control site samples mean that stratification was not observed away from the AR. One year after AR deployment (Figure 4b) near bottom and euphotic water samples showed high affinity for organic nitrogen and phosphorus, which are well represented in positive axis 1 and 2. In contrast, euphotic control site samples show maximum affinity to photosynthesis related parameters (DO and pH) which had the highest contribution in negative axis 2.

May: spatial variability – A well-defined stratification down the water column between near bottom and euphotic water samples both for AR and control site results from the high variance among samples during this month (Figure 5a). AR near bottom water reaches maximum affinity to nutrients and organic compounds, which are well represented in negative axis 1 and 2. Photosynthesis related parameters (Chl *a*, Phaeop, DO, pH) highly represented in positive axis 1 show the maximum affinity with AR and control site euphotic water samples. A similar pattern was observed one year later (Figure 5b) reflecting intense photosynthetic activity in superficial waters. Silicate availability and chlorophyll *a* high concentrations ($6 \mu\text{M}$ and $3 \mu\text{g L}^{-1}$, respectively), probably due to diatoms development during the Spring period reinforced the previous mentioned results. Nutrients and organic dissolved compounds that reach maximum representation in negative axis 1 led to a high affinity with near bottom water samples.

August: spatial variability – An evident contrast was observed between AR near bottom water and control samples in August (Figure 6a). AR near bottom water samples are well represented in the negative axis 1 showing affinity with Si(OH)_4 , HPO_4^{2-} , NH_4^+ and DON, in contrast to AR euphotic water samples, possibly due to biological nutrient consumption in surface waters. A similarity among all control site water samples,

closely associated with pH, Chl *a* and NO_3^- was observed showing no stratification at AR control areas. One year later (Figure 6b), a high variance between near bottom and euphotic water samples was observed both for AR and control site water samples, pointing to a well-defined stratification along the water column. Organic dissolved compounds and photosynthesis related parameters (DO, pH, Chl *a*) affinity with euphotic water samples was the most important result observed in August. The near bottom water samples were closely associated with nutrients (NH_4^+ , NO_3^- and Si(OH)_4) well represented in positive axis 1.

November: spatial variability - The highest variance between AR and control site water samples was observed in November (Figure 7a). The DON, NH_4^+ , NO_3^- , HPO_4^{2-} , Si(OH)_4 , DO, Chl *a* and pH, highly represented in positive axis 1, were closely associated with AR near bottom water samples pointing to a clear environmental difference between the AR and control site. The same spatial pattern was found one year later (Figure 7b), emphasising the association between environmental parameters and all AR samples.

DISCUSSION

Artificial reef structures enhance settlement of organic matter in the seabed with the biological and chemical degradation of dead plants and animals leading to benthic remineralization (Ambrose & Anderson, 1990; Lomstein et al., 1989; Rizzo, 1990).

These findings may explain the rate of organic carbon accumulation in AR seabed ($14 \mu\text{g g}^{-1} \text{ month}^{-1}$). In fact, a linear relationship ($\text{TOC} = 14.3\text{m}^{\text{th}} - 20.5$; $r^2 = 0.4$; $n = 19$; $p < 0.05$) was obtained for TOC upper sediment layer over the period of study. Although an accumulation of TOC in the upper sediment layer was observed, the highest

concentrations were recorded in the sub-layer (ANOVA; $n= 19$; $p< 0.01$). This may be due to hydrodynamic disturbance (winds, waves, and tidal currents) on topmost sediment that easily lose incorporated organic material. A significant exponential fit between TOC and Chl *a* ($r^2= 0.91$; $n= 19$; $p< 0.01$) indicates a relationship between the sub-layer high TOC concentrations and benthic productivity. Such results were also reported in a study on a benthic-pelagic coupling system, indicating that fresh organic input result in benthic activity enhancement (Gutiérrez et al., 2000). As animal metabolic activities and decomposition processes may be transforming large quantities of particulate nitrogen into dissolved-reduced forms (Dame et al., 1986), the extremely low levels of organic nitrogen found in the seabed beneath the reef may be due to rapid turned over of nitrogen.. It is known that HPO_4^{2-} released from organic material is almost completely retained in sediment due to an early diagenetic “sink-switching” to authigenic carbonate fluorapatite (Ca-bound P) and to Fe-bound P (Slomp, 1997). This could explain the relatively constant level of organic phosphorus in AR seabed over the two-year period, since phosphorus may be transferred to lithogenic particles (Ca and Fe), being Fe-bound P an intermediate chemical structure between organic phosphorus and carbonate fluorapatite [$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3\text{F}$], the most important source/sink for reactive dissolved phosphorus (Slomp, 1997).

It is known that artificial reefs enhance planktonic communities due to changes in water flow and turbulence patterns, bringing more plankton to bottom waters and promoting recycling of benthic nutrients (Haroun et al., 1994; Ambrose & Anderson, 1990). Planktonic communities development in the AR surrounding environment are in accordance with POC, PON and POP time evolution. This fact highlights a clear pattern with lowest concentrations before AR submersion, followed by pulse increases during

2003 and 2004 Spring/Summer periods. Six months after AR deployment the origin of settled particles became clear due to biogenic material pull-out within a short time scale. At the deployment stage high C/N and low N/P ratios were both abnormal (236 and 0.4, respectively). The reasons for such a phenomenon may be related to scarcity of biogenic material and fast nitrogen degradation, in relation to carbon and phosphorous. Nitrogen concentrations tended to decrease to zero, leaving a small phosphorous concentration. Other authors have shown that nitrogen is the most important nutrient in limiting phytoplankton growth in open sea (Ryther & Dunstan, 1971; Codispoti, 1989).

Artificial reefs have the capacity to promote biological production due to high availability of nutrients in the water column (Relini et al., 1994; Perkol-Finkel & Benayahu, 2005). The highest concentrations of ammonium, nitrates, phosphates, silicates and organic nitrogen were observed in the reefs' near bottom water, in contrast to euphotic waters due to phytoplankton uptake in surface waters. In fact, higher values of chlorophyll *a* ($2.7\mu\text{g g}^{-1}$) and pH (8.8) were observed in the AR and control site euphotic water mainly during Spring period. This may reflect photosynthesis effect, since micro and nanophytoplankton densities seasonal cycle are higher during Spring/Summer (Nuccio et al, 2003), due to nutrient availability and primary production pattern in coastal waters (Fiala et al., 2002). Water temperature seems to play an important role in chemical and biological changes down the water column during the summer, since biological activity within euphotic zone may induce organic material production by exudation and excretion. This could explain the highest concentrations of dissolved organic compounds in euphotic water observed in August (2004). In this period, dissolved organic nitrogen was 20 % higher in the euphotic zone than near the bottom. Within the AR, water enrichment became more evident in November (2004),

showing higher percentages of ammonium (30 %), nitrates (21 %), silicates (70 %), DON (33 %), Chl *a* (30 %) and Phaeop (77 %), than at the control site, suggesting that two years after reef deployment chemical changes may be reflected in the water column. Control site oligotrophic waters contrast with reef water emphasizing the role of substratum composition in water column nutrient enrichment. Similar findings were described in other oceanographic studies over the continental shelf in central Adriatic coast (Fabi & Fiorentini, 1994), Scotland (Wilding & Sayer, 2002) and Canary Islands (Haroun et al., 1994).

According to other worldwide studies, artificial reef deployment has resulted in original community enrichment and diversification, increasing biotic and abiotic habitat complexity, ecological niches and food webs on a local scale (Relini et al., 1994; Fabi & Fiorentini, 1994; Ambrose & Anderson, 1990). The present study shows a trophic chain pull out due to nutrients, biogenic particles and microphytobenthos enrichment two years after the deployment of the Faro/Ancão artificial reef. The organic sediment enhancement and water nutrient enrichment within the reef system reinforces the importance of these man-made structures as a potential tool in the modification of coastal ecosystems as described by Pickering et al. (1998).

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TABLES CAPTIONS

Table 1 – Concentrations (mean \pm *sd*) of total organic carbon (TOC), total inorganic carbon (TIC), weakly bound-P, Fe-bound P, Ca-bound P and total organic phosphorus (TOP), within the sediments of the artificial reef (A₁₀), from Summer 2002 to Summer 2004.

Table 2 - Concentrations (mean \pm *sd*) of particulate organic carbon (POC), particulate organic nitrogen (PON) and particulate organic phosphorus (POP), in the settled particles of sediment traps within the artificial reef from Summer 2002 to Summer 2004.

FIGURES CAPTIONS

Figure 1 - Location of the Faro/Ancão artificial reef off Faro (Algarve, southern Portugal) with the sampling station (A₁₀). Scheme of the reef and perspective view of the concrete blocks.

Figure 2 - Values of C/N ratio in settled particles from Summer 2002 to Summer 2004.

Figure 3 - Values of N/P ratio in settled particles from Summer 2002 to Summer 2004.

Figure 4_(a,b) – Principal Component Analysis ordination plots of physical (DO, pH), chemical (NH₄⁺, NO₃⁻, HPO₄²⁻, Si(OH)₄, DON, DOP) and biological (Chl *a*, Phaeop)

parameters (concentration range) in water column within the AR (●- 0.5 m; ■- 10m; ▲- 20m) and C-control site (○-0.5 m; □-10 m; △-20m), in February (2003 and 2004).

Figure 5_(a,b) - Principal Component Analysis ordination plots of physical (DO, pH), chemical ($(\text{NH}_4^+$, NO_3^- , HPO_4^{2-} , $\text{Si}(\text{OH})_4$, DON, DOP) and biological (Chl *a* and Phaeop) parameters (concentration range) in water column within the AR (●- 0.5 m; ■- 10m; ▲- 20m) and C-control site (○-0.5 m; □-10 m; △-20m), from May (2003 and 2004).

Figure 6_(a,b) - Principal Component Analysis ordination plots of physical (DO, pH), chemical ($(\text{NH}_4^+$, NO_3^- , HPO_4^{2-} , $\text{Si}(\text{OH})_4$, DON, DOP) and biological (Chl *a* and Phaeop) parameters (concentration range) in water column within the AR (●- 0.5 m; ■- 10m; ▲- 20m) and C-control site (○-0.5 m; □-10 m; △-20m), from August (2003 and 2004).

Figure 7_(a,b) - Principal Component Analysis ordination plots of physical (DO, pH), chemical ($(\text{NH}_4^+$, NO_3^- , HPO_4^{2-} , $\text{Si}(\text{OH})_4$, DON, DOP) and biological (Chl *a* and Phaeop) parameters (concentration range) in water column within the AR (●- 0.5 m; ■- 10m; ▲- 20m) and C-control site (○-0.5 m; □-10 m; △-20m), from November (2003 and 2004).

Table 1-

	Layer	TOC	TIC	Wb-P	Fe-bound P	Ca-bound P	TOP	Chl <i>a</i>
	cm	$\mu\text{mol g}^{-1}$	$\mu\text{mol g}^{-1}$	$\mu\text{mol g}^{-1}$	$\mu\text{mol g}^{-1}$	$\mu\text{mol g}^{-1}$	$\mu\text{mol g}^{-1}$	$\mu\text{g g}^{-1}$
Summer-02	0-1	5 ± 0.7	774 ± 252	0.14 ± 0.022	0.59 ± 0.331	0.65 ± 0.283	1.95 ± 0.152	0.38 ± 0.041
	1-2	442 ± 162	586 ± 169	0.14 ± 0.021	0.69 ± 0.519	0.8 ± 0.152	2.54 ± 0.283	0.56 ± 0.200
Autumn-02/Winter-03	0-1	49 ± 15	720 ± 124	0.15 ± 0.030	0.71 ± 0.213	0.64 ± 0.164	1.71 ± 0.164	0.12 ± 0.049
	1-2	331 ± 140	887 ± 349	0.16 ± 0.041	0.78 ± 0.133	0.57 ± 0.222	2.35 ± 0.222	0.15 ± 0.065
Spring-03/Summer-03	0-1	308 ± 176	1169 ± 113	0.12 ± 0.020	0.66 ± 0.334	1.66 ± 0.155	1.52 ± 0.185	0.63 ± 0.504
	1-2	556 ± 303	1122 ± 292	0.13 ± 0.040	0.75 ± 0.070	0.67 ± 0.185	2.58 ± 0.155	0.92 ± 0.592
Autumn-03/Winter-04	0-1	113 ± 68	1019 ± 221	1.24 ± 0.056	0.70 ± 0.250	0.6 ± 0.279	1.21 ± 0.190	0.19 ± 0.059
	1-2	243 ± 125	439 ± 257	1.26 ± 0.052	0.74 ± 0.279	0.63 ± 0.250	1.80 ± 0.161	0.22 ± 0.068
Spring-04/Summer-04	0-1	459 ± 113	936 ± 191	0.19 ± 0.058	1.58 ± 0.647	1.58 ± 0.198	1.36 ± 0.198	0.82 ± 0.449
	1-2	1090 ± 550	1021 ± 103	0.23 ± 0.052	1.80 ± 0.627	1.8 ± 0.092	1.88 ± 0.092	1.18 ± 0.618

Table 2 -

	Summer-02	Autumn-02/Winter-03	Spring-03/Summer-03	Autumn-03/Winter-04	Spring-04/Summer-04
	$\mu\text{mol g}^{-1}$	$\mu\text{mol g}^{-1}$	$\mu\text{mol g}^{-1}$	$\mu\text{mol g}^{-1}$	$\mu\text{mol g}^{-1}$
POC	590 ± 253	773 ± 361	2330 ± 182	986 ± 594	3292 ± 410
PON	2.5 ± 1.62	47 ± 31	241 ± 30	77 ± 46	178 ± 57
POP	5.9 ± 1.07	5.5 ± 3.93	11.7 ± 3.06	5 ± 2.1	8.3 ± 2.61

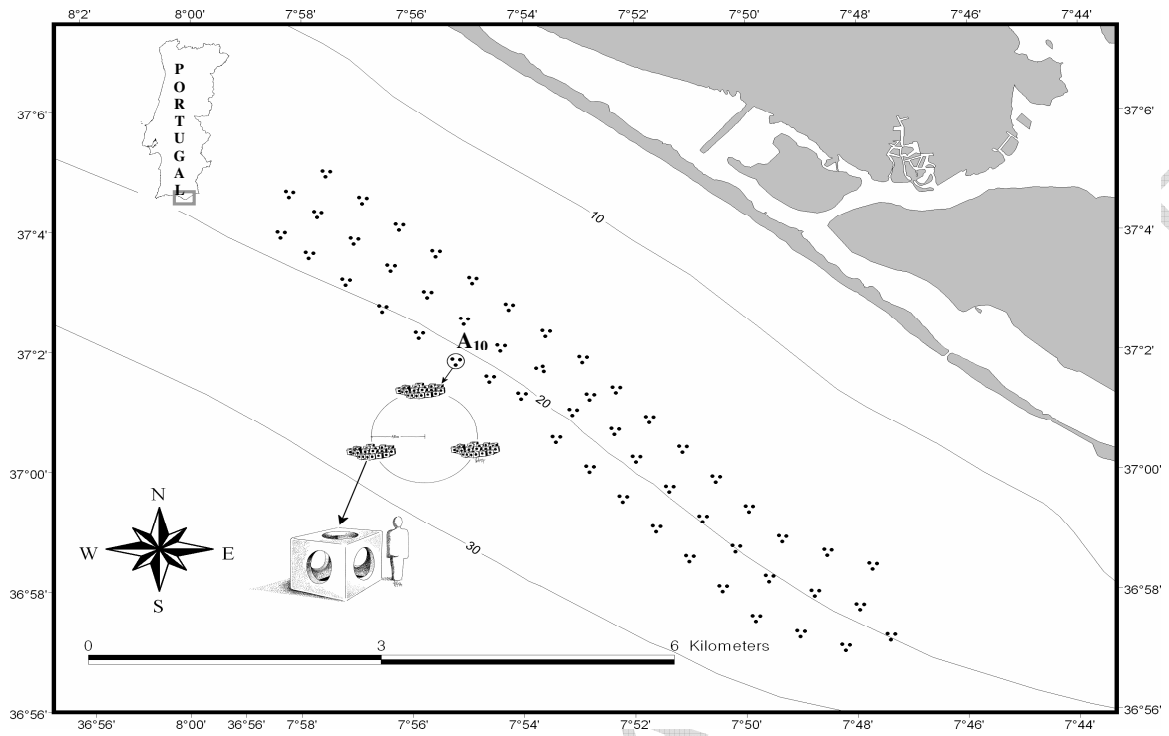


Figure 1-

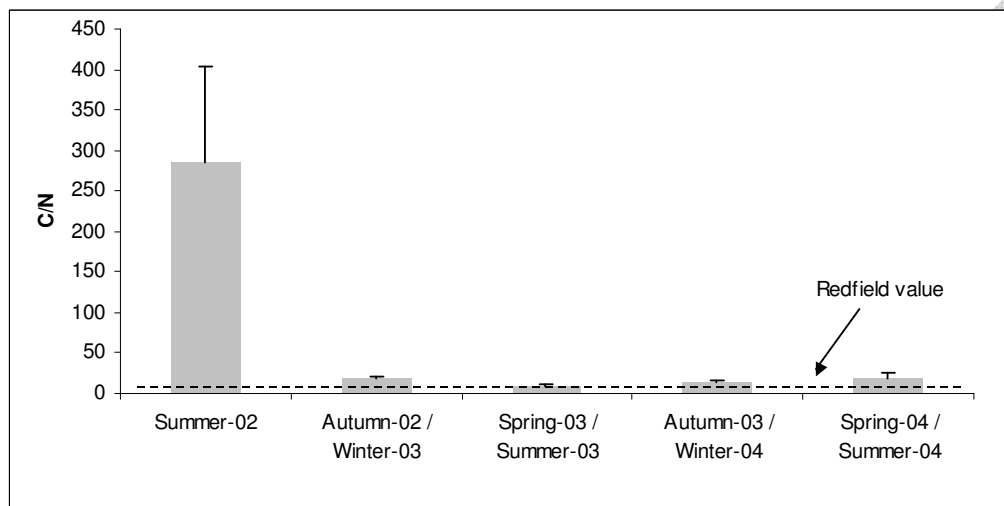


Figure 2 -

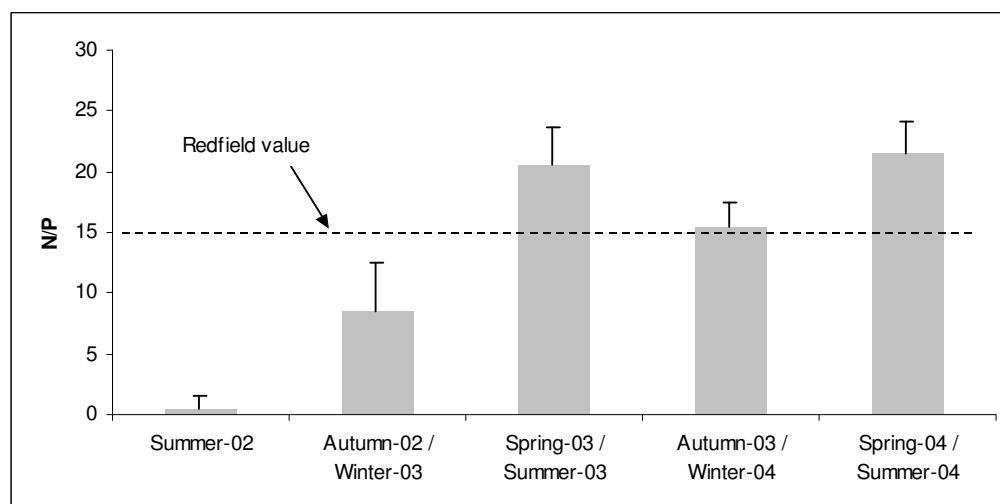
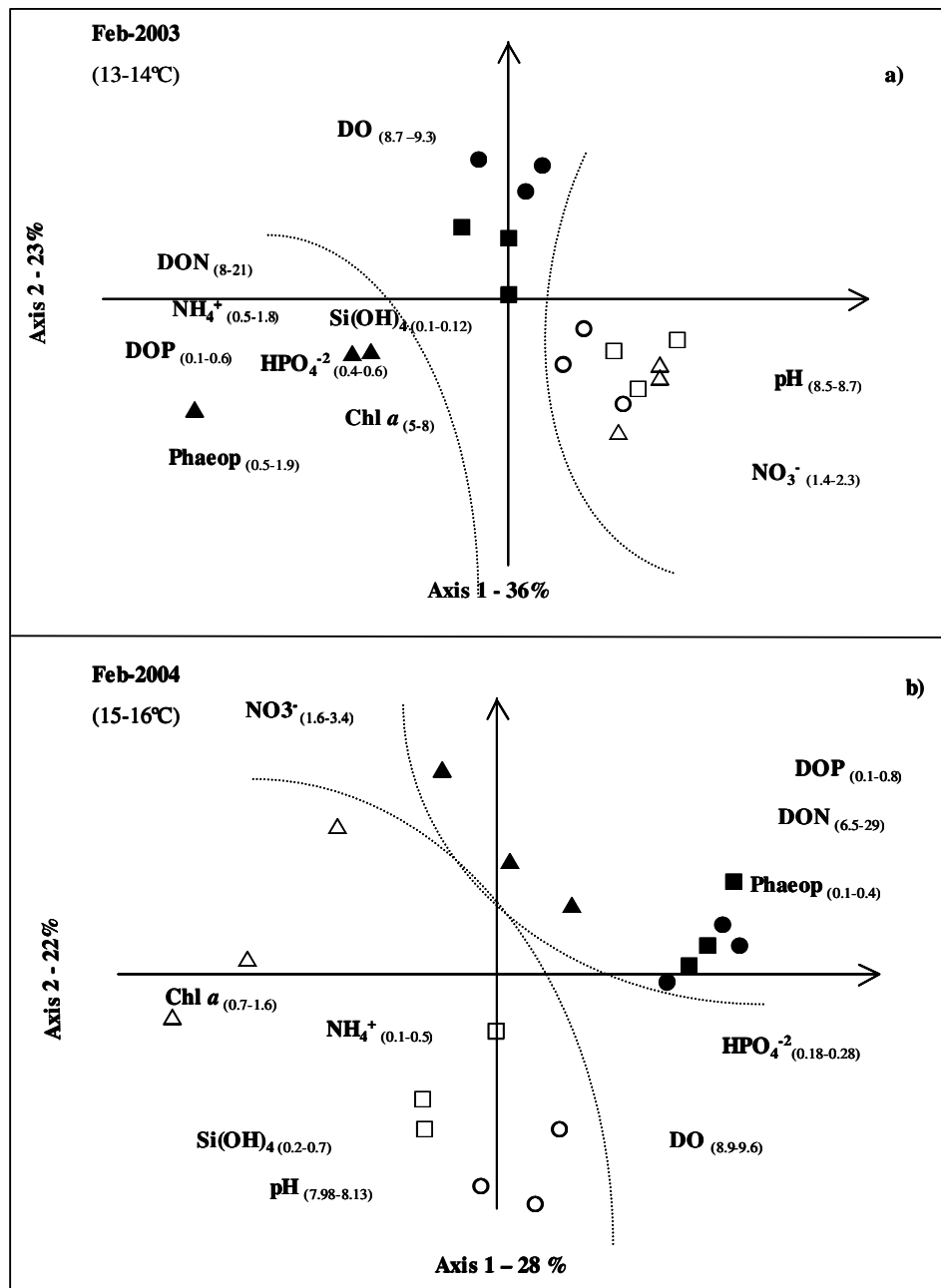
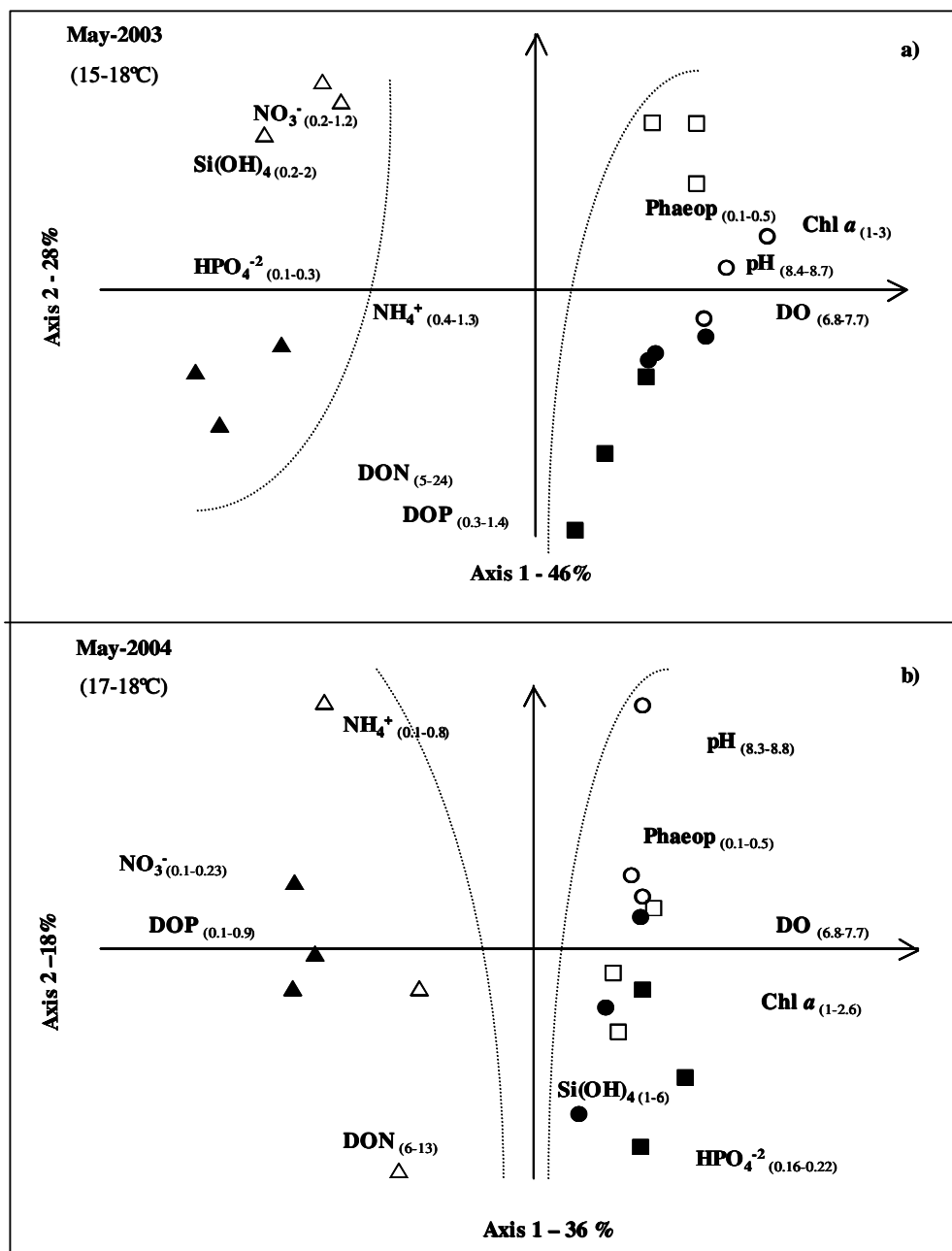


Figure 3 -

Figure 4_(a,b) -

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Figure 5_(a,b) -

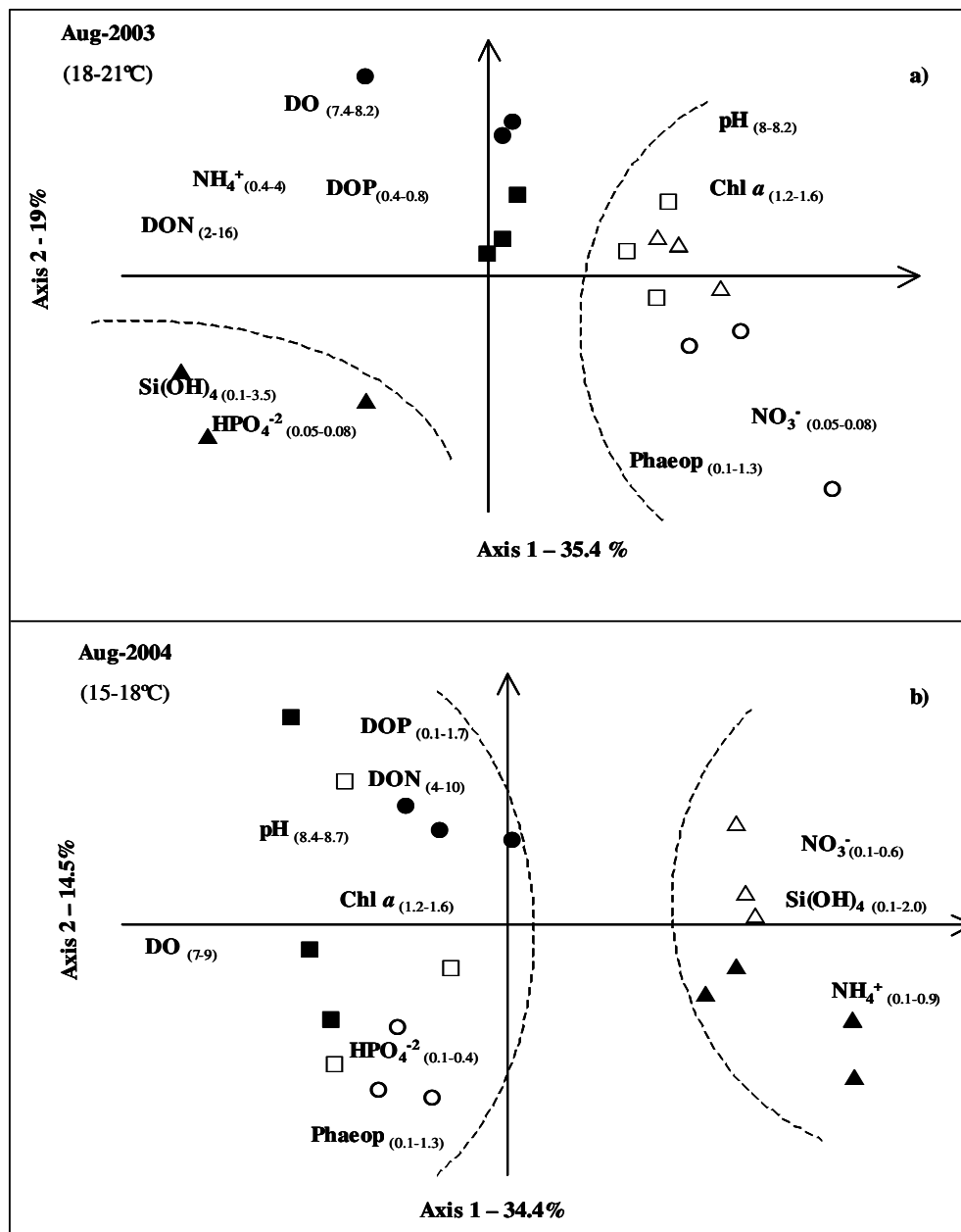
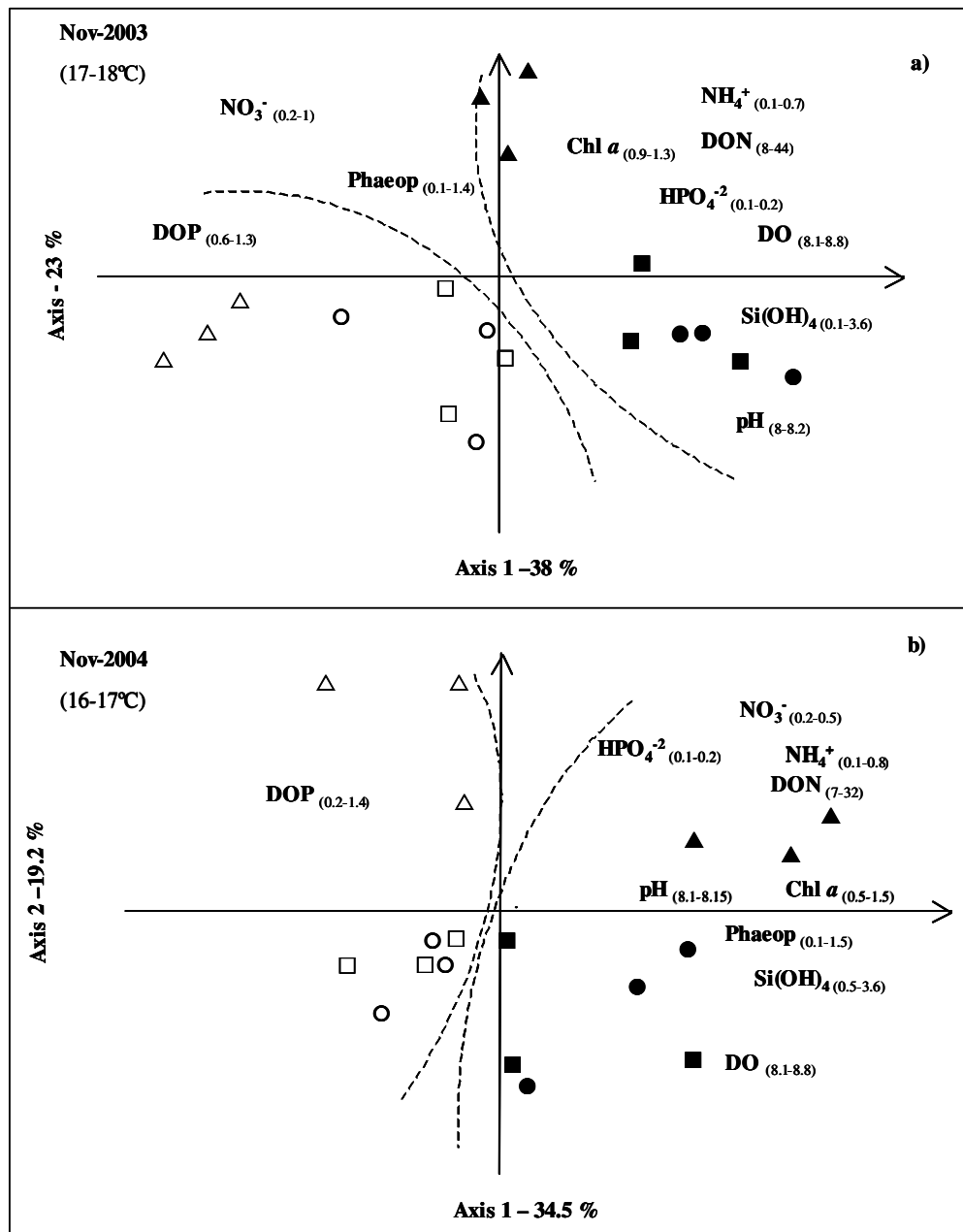


Figure 6(a,b) -

Figure 7_(a,b) -

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