J. Appl. Environ. Biol. Sci., 6(7)109-124, 2016

ISSN: 2090-4274
Journal of Applied Environmental and Biological Sciences
www.textroad.com

Distribution of Nitrogen, Phosphorus and Silicon in The Gulf of Annaba North-East of Algeria

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Received: March 3, 2016
Accepted: May 18, 2016

ABSTRACT

In order to assess the temporal and spatial distributions of nutrients in the Gulf of Annaba under the influence of estuaries inputs, from January 2010 to December 2012 monthly samples of both surface and bottom waters were collected from six stations in the Gulf and from two stations in the estuaries of Seybouse and Mafragh wadis. Nitrogen, Phosphate, Silicates, Biogenic Silica and Chlorophyll *a* in the Gulf as well as flux and surface waters nutrient concentrations in the wadi outlets were measured. In Seybouse outlet, levels of Total Dissolved Nitrogen reached an average of 63 $\mu mol.l^{-1}$, and proportionately Dissolved Organic Nitrogen 15%, NO_3 25% and NH_4 54%. These values indicate that Seybouse estuary is a major anthropogenic source influencing the chemistry of the Gulf of Annaba. Most of the silicon (>70%) in the Gulf is as silicate (SiO_4) while Biogenic Silica represents a minor percentage (12%). On the other hand, a relatively high Chlorophyll *a* value (7 $\mu g.l^{-1}$) is recorded in the waters of the inner Gulf. Total Dissolved Nitrogen fluxes varied from 370 $t.y^{-1}$ in Mafragh estuary to 900 $t.y^{-1}$. In Seybouse estuary, Dissolved Inorganic Nitrogen (DIN) ranged from 64% to 83%. In addition to the strong loadings introduced into the Gulf, mainly through Mafragh wadi, the loading ratios DIN:PO_4 (>30) and SiO_4:DIN (<1) are unbalanced, suggesting that Phosphate and Silicon are as limiting factors in the growth of phytoplankton in the coastal waters of the Gulf.
KEYWORDS: Nutrient; Flux; Silicates; Estuary; Coastal Waters, Annaba Gulf, Mediterranean Sea.

1. INTRODUCTION

The Mediterranean Sea is considered as a hot spot for both littoral and marine biodiversity [1, 2, 3]. Many studies [4, 5, 6, 7, 8, 9] give evidence that the Mediterranean, affected by human settlements, is becoming one of the most endangered marine ecosystems on earth. Although that the coastal areas contribute to economic growth through fisheries, aquaculture and tourism, they are also very sensitive to diverse anthropogenic activities. They need to be monitored, preserved and protected in order to insure a sustainable social and economical development [10, 11, 12]. As regards the multiple and uncoordinated use of water in the industrial areas, agricultural irrigation and urban needs, despite the climate change effects, river discharges in the Mediterranean area became a worrying matter [13, 14]. During recent decades, anthropogenic factors have resulted, within the drainage basins of many rivers, in drastic changes of the dissolved and particle properties of waters flowing into the sea [15].

Moving eastward, the Modified Atlantic Water current (MAW), crosses the shelf of Annaba allowing the renewing of outer neritic waters. The Gulf of Annaba receives nutrients from Seybouse and Mafragh wadis and from various sources, including Annaba urban wastewaters and industrial discharges. The areas around Seybouse and Mafragh wadis are densely populated (over 220 inhab/km²). The littoral area of Annaba is one of the largest industrial parks of Algeria with more than 206 factories, including *El Hadjar Iron and Steel Complex* and *Fertial* fertilizer factory [16]. The latter factory discharges, directly into the Gulf, wastewaters strongly loaded with ammonium ions and phosphate waste. Becoming more intensive, the agricultural activity is the main land use and the watersheds are largely regulated by many dams retaining nearly the third (Mafragh) to the half (Seybouse) of the total annual runoff. Mafragh watershed is characterized by its large virgin wetlands in its lower part that acts as a buffer area for contaminants and preventing flooding events. In contrast, industrialization of the northern part of the Seybouse basin, high population density and intensive agriculture make Seybouse wadi as one of the most heavily polluted wadis in the country.

However, data on river nutrient loadings to the Mediterranean basin is also scarce, otherwise missing in many eastern and North African countries [15, 17, 18]. In Algeria, few studies were performed on the

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distribution of dissolved nutrients in wadis in relation to coastal inputs [19, 20, 21, 22]. Concerning the Gulf of Annaba, published data are very limited in time and space dealing with the distribution of inorganic nitrogen and phosphate in the inner sector of the Gulf [23, 24]. Still, works on the spatial and temporal distribution and fluxes of N, P and Si in coastal waters in Algeria are nonexistent with the exception of two works on the seasonal fluxes of inorganic N and PO_4 from the Mafragh estuary outlet [25, 26].

This work deals with the measurements of nutrient concentrations of Nitrogen, Phosphate, Silicates, Biogenic Silica and Chlorophyll *a* in order to evaluate the spatial and temporal distribution of nutrient concentrations in the Gulf of Annaba under the influence of inputs from both Mafragh and Seybouse estuaries.

2. MATERIALS AND METHODS

Sampling sites and procedures

According to the importance of external influences and hydrodynamic features as well as to the specific hydrographic characteristics of the Gulf of Annaba, eight sampling stations were fixed in three areas:

- Four stations (**S1**, **S2**, **S3, S5**) in the outer waters of the Gulf located far from the continental influence and mostly under MAW intrusion,
- Two stations (**S4, S6**) in the inner waters (estuaries plumes) submitted to the Seybouse and Mafragh inputs that plays a crucial role in the adjacent coastal ecosystem [19, 26],
- Two stations (**S7, S8**) in each of the wadi outlet (**Fig. 1**; **Tab.1**).

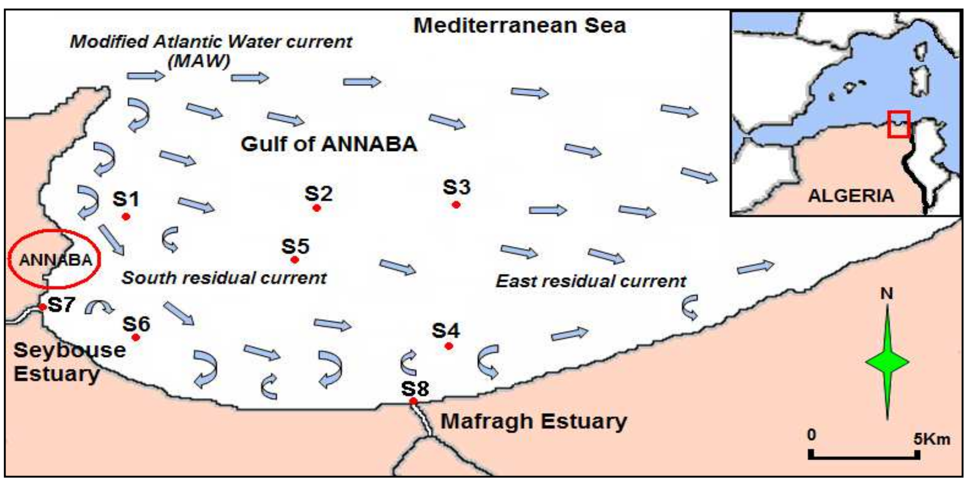

Figure 1: Sampling stations and dominant currents in the Gulf of Annaba.

In order to assess the temporal and spatial distributions of nutrients in the Gulf under the influence of the two estuaries inputs, from January 2010 to December 2012, both surface and bottom waters were monthly sampled from the six stations **S1**, **S2**, **S3**, **S4**, **S5** and **S6** for measurement of Nitrogen, Phosphate, Silicates, Biogenic Silica and Chlorophyll *a*. Fluxes and nutrient concentrations in the surface waters were measured in the wadis outlets (**S7**, **S8**). From 2011 to 2012, Biogenic Silica was measured in **S1**, **S2**, **S3**, **S4**, **S5** and **S6**. Owing to bad weather during March 2010 and January 2012, samples from the Gulf stations (**S1** to **S6**) were not collected.

Table 1: Geographical coordinates and characteristics of the sampling stations.

Stations	Latitude ; Longitude	Sampling Depth (m)	Bottom
S1	07° 48’ 33”**E** ; 36° 54’ 93”**N**	27	Mud
S2	07° 53’ 39”**E** ; 36° 55’ 25”**N**	42	Mud
S3	07° 58’ 04”**E** ; 36° 54’ 41”**N**	40	Mud
S4	07° 58’ 12”**E** ; 36° 51’ 92”**N**	19	Sand
S5	07° 53’ 60”**E** ; 36° 52’ 72”**N**	26	Rock-Mud
S6	07° 47’ 13”**E** ; 36° 51’ 85”**N**	15	Sand
S7	07° 46’ 23”**E ;** 36° 52’ 03”**N**	Surface water	Sand-Mud
S8	07° 56’ 41”**E ;** 36° 50’ 49”**N**	Surface water	Sand-Mud

Water salinity and temperature were measured with a multi-parameter probe (WTW 197i), and bottom waters sampled with a Niskin bottle. From the middle of the flow of Seybouse and Mafragh estuaries (**S7**, **S8**), two liters of water were collected for nutrient analysis, frozen in polyethylene bottles then processed within two days after collection.

Analytical methods

After filtration through Whatman GF/C glass filters (0.5µm porosity), nutrient contents of phosphate PO_4, ammonia NH_4, nitrate NO_3, nitrite NO_2, silicates SiO_4, Total Dissolved Nitrogen (TDN), Dissolved Organic Nitrogen (DON) and Dissolved Inorganic Nitrogen (DIN) (i.e. Ammonia NH_4; nitrate NO_3; nitrite NO_2) was measured through standard calorimetric methods according to Parsons et al. [27]. Total Dissolved Phosphorus (TDP), Dissolved Inorganic Phosphorus (DIP) and Dissolved Organic Phosphorus (DOP) were measured following the standard method of [28]. Freshwater flow (in $m^3\ s^{-1}$) is estimated by multiplying the water velocity ($m\ s^{-1}$) by the total surface area (m^2) of the wadi wet section and the instantaneous flux of nutrients by multiplying their concentrations by the estuary flow. Annual load of nutrients is assessed with the method of average instantaneous loads [29], and particulate matter and Biogenic Silica (BSi) using a double extraction method as described in the literature [29, 30, 31]. For measurements of Chlorophyll *a* (Chl *a*) (using a GF/C filter 0.5µm), samples were preserved and analyzed as indicated by Strickland and Parson [32].

Statistical analysis

Statistica 2008 software (Version 8.0.550) was used to perform multivariate Correspondence Analysis (CA) in order to verify the possible co-variations of the inorganic nutrients in the two estuaries outlets (**S7**, **S8**) and the coastal stations (**S1** to **S6**) during the three year survey. The contingency table analyzed with CA is a matrix of the annual averages of 11 nutrient levels and ratios (variables) observed on 24 spatiotemporal situations (objects) representing the two estuaries outlets.

3. RESULTS

Nutrient variability and fluxes at the estuaries outlets

Seybouse outlet waters are highly charged with dissolved nitrogen forms (DIN = NH_4 + NO_2 + NO_3) and phosphate (PO_4), and whose levels are higher than in Mafragh estuary (**Tab.2**). Nitrate (NO_3) concentrations largely varied with the seasons (0.2 to 38 $\mu mol.l^{-1}$) with an annual average of 12 $\mu mol.l^{-1}$, but globally remaining elevated (2.7 to 38 $\mu mol.l^{-1}$) during the wet season. However, NO_3 amounts decreased during the dry season (0.2 to 25 $\mu mol.l^{-1}$) owing to the domination of the low nitrate marine water intrusion as well as to the significant reduction of freshwater inflow.

The seasonal evolution of NO_2 follows, particularly that of nitrate, constitutes a small convertible stock (about 10%) of dissolved inorganic nitrogen. According to the year, the main characteristic of Seybouse wadi is its large ammonium (NH_4) levels reaching 54 to 88 $\mu mol.l^{-1}$. This represents more than 18-fold the levels recorded in Mafragh outlet. During the dry season, Seybouse estuary is rich in NH_4 with an average of 17-52 $\mu mol.l^{-1}$. Seybouse outlet shows abundant concentrations of NH_4 which paradoxically increase by 35% during the dry season. Oxidized forms of nitrogen (NO_3 and NO_2) generally occur in a low fraction compared to NH_4 which proportion is over 80 % of the DIN. In Mafragh outlet, nitrogen oxidized form is about 55 % in contrast to Seybouse estuary. Similarly to the nitrogen dynamics, Seybouse estuary shows high levels in PO_4 with values ranging from 2.7 to 5.3 $\mu mol.l^{-1}$, and a maximum record during 2010. Relatively to Mafragh, the enrichment of Seybouse waters in PO_4 is several fold higher. In Mafragh, the average levels ranged from 1 to 2 $\mu mol.l^{-1}$ with a maximum of 3.5 $\mu mol.l^{-1}$ recorded in 2010 during the wet season. In Seybouse outlet, TDN levels reach an average of 63 $\mu mol.\ l^{-1}$, with DON 15 %, NO_3 25 % and NH_4 54%. In Seybouse waters, the TDP major component is DOP with 52 %.

At Mafragh outlet, levels of TDN range between 5 and 90 $\mu mol.l^{-1}$, with an average of 36 $\mu mol.l^{-1}$. Dissolved organic fraction forms reach 41% of TDN at the opposite of Seybouse waters where nitrogen inorganic form proportions are 25% for NO_3 and 28% for NH_4. For dissolved phosphorus, inorganic form levels are dominant (53%) with a mean of 2 $\mu mol.l^{-1}$ while PO_4 proportion is only 3%. In the estuary, Dissolved Organic Nitrogen (DON) strongly varied from 0.3 to 60 $\mu mol.l^{-1}$ between the seasons with a mean values ranging from 6 to 20 $\mu mol.l^{-1}$. However, SiO_4 levels, in contrary to DIN forms and PO_4, are found low in the two estuaries particularly in the dry period where the average values decreased to 15 $\mu mol.l^{-1}$ in 2012.

Estuaries Nutrient fluxes vary strongly from year to year, depending mainly on the wadis flows. The estuarine flows, at the respective outlets, fluctuate according to rainfall levels and mostly in Seybouse estuary. In the latter, water discharges during 2012 are 3 fold higher than those of 2010 and 2011. Indeed, the minimum levels of flow records in 2010 and 2011 are due to the low amounts of rainfall affecting the whole Seybouse basin. Details of records of nutrient variability in the two estuaries are in Figure 2. TDN fluxes varied in the range of 2-fold from 370 t/y in Mafragh to 900 t/y in Seybouse estuary where DIN proportions vary from 64% to 83% in contrast to values expressed in terms of levels. Exceptionally, Si-SiO_4 fluxes are higher in Mafragh than in Seybouse estuaries. Beside, the loading ratios DIN:PO_4 and SiO_4:DIN are unbalanced; N:P ratio is above 5 and SiO_4:DIN ratio is below 2.

Table 2: Nutrient fluxes (t/yr) inputs (Jan. 2010 to Dec. 2012) from Seybouse and Mafragh estuaries into the Gulf of Annaba with the Redfield molar ratios **N:P** and **Si:N**.

	SEYBOUSE			MAFRAGH		
	2010	2011	2012	2010	2011	2012
Average Annual Flow ($m^3 s^{-1}$)	16	17	43	25	45	58
TDN	911	1 200	1 139	494	583	647
DIN	780	1 013	1 008	318	368	424
DON	132	187	140	163	214	223
N-NH_4	474	554	481	153	165	192
N-NO_3	248	362	428	132	158	176
N-NO_2	58	97	99	57	45	55
TDP	225	263	371	118	105	148
DIP	119	138	175	75	49	65
DOP	104	125	197	46	56	83
P-PO_4	105	126	161	46	30	44
Si-SiO_4	732	971	1 605	1 188	2 136	2 421
N:P (DIN:P-PO_4)	7.4	8.0	6.3	7.7	12.3	9.6
Si:N (Si-SiO_4 : DIN)	0.9	1.0	1.6	3.4	5.8	5.7

Abbreviations: Total Dissolved Nitrogen (TDN); Dissolved Inorganic Nitrogen (DIN); Dissolved Organic Nitrogen (DON); Total Dissolved Phosphorus (TDP); Dissolved Inorganic Phosphorus (PID); Dissolved Organic Phosphorus (DOP); Phosphate (PO_4); Silicon (Si); Silicates (SiO_4); Dissolved Organic Phosphorus(DOP).

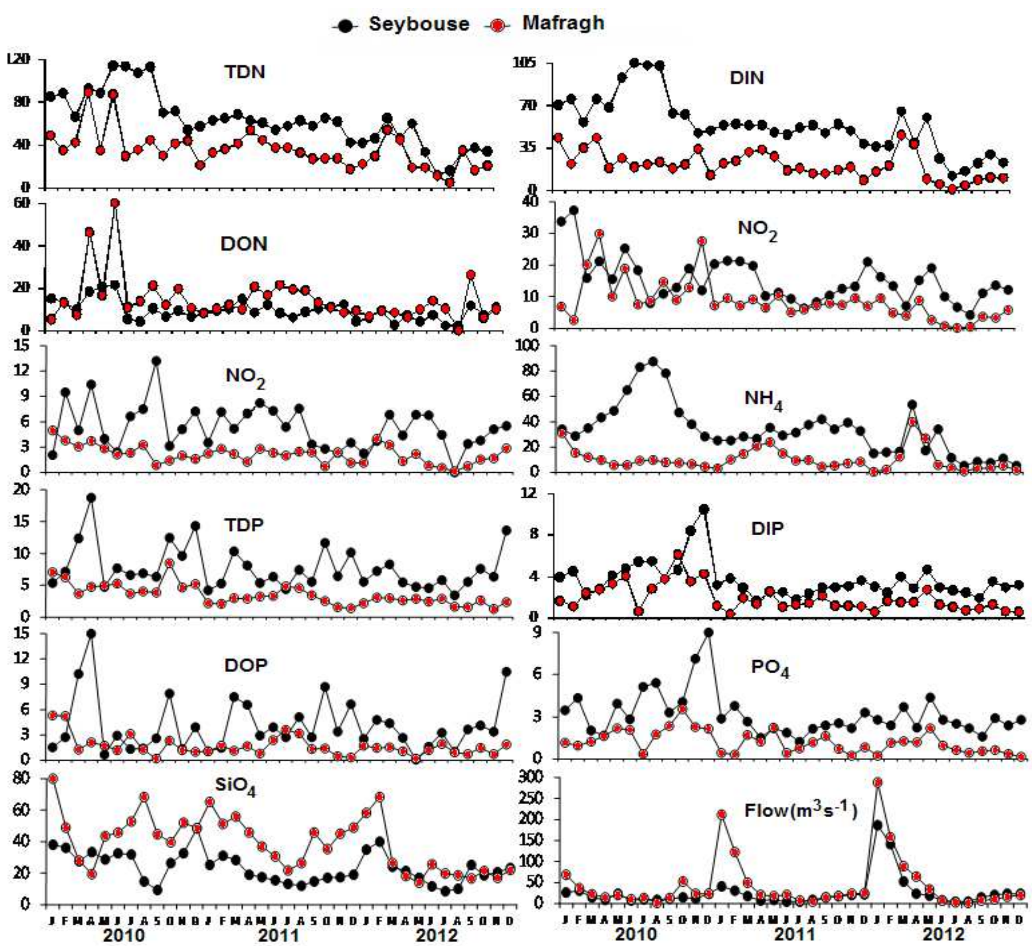

Figure 2: Variations of nutrient levels (µmol l^{-1}) and flow in the Seybouse and Mafragh estuaries (January 2010 to December 2012).

Hydrology and nutrient variability

The water temperature ranged from 12°C in February to 30°C in August with average values from 19°C to 23°C depending on the station. All along the years of samplings, surface salinity fluctuated between 28 and 38. The low salinity record is close to Seybouse plume in **S6** (27.7 to 37.2). In the inner station **S4** near Mafragh plume, surface values range from 32 to 37.5 (**Fig.3**).

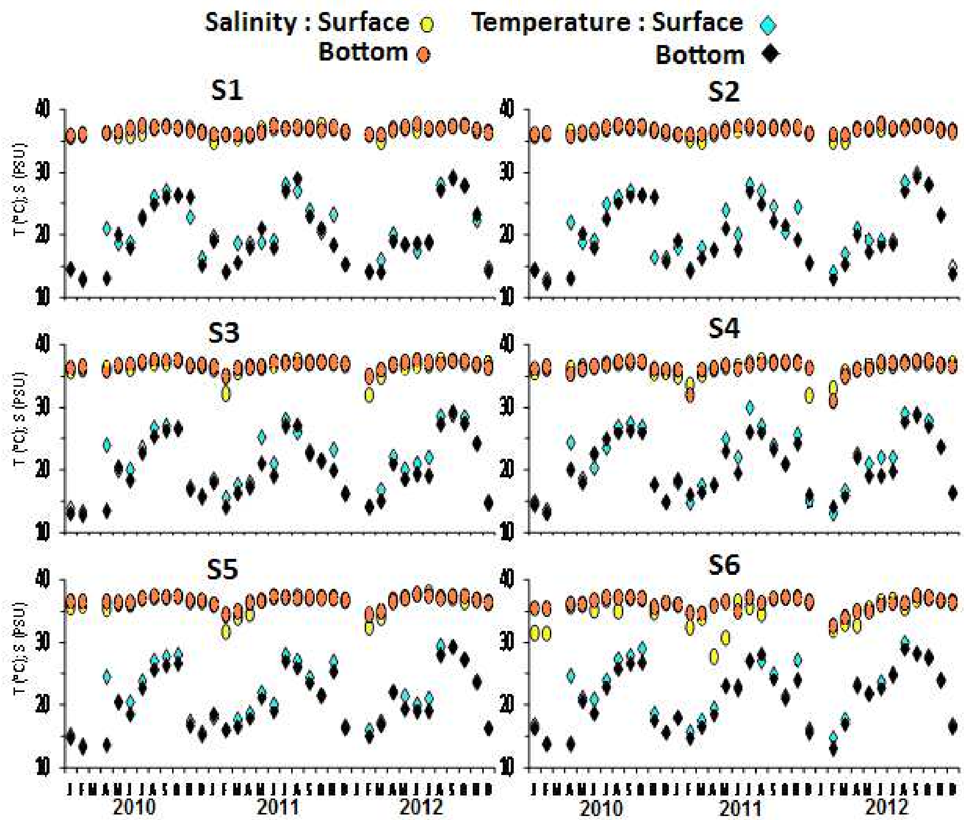

Figure 3: Variations of temperature and salinity in the six stations of the gulf of Annaba (January 2010 to December 2012).

From 2010 to 2012, TDN values in the Gulf stations reach in average 14 µmol.l^{-1} but oscillated within the range of 6 to 42 µmol.l^{-1} (**Fig.4a,4b**), with TDN components reaching 60% (DON), 22% (NO_3) and 13% (NH_4). During that period, levels of DIN in the surface waters remained unchanged fluctuating around 10 µmol.l^{-1} in the Seybouse plume where NO_3 proportions of the main DIN fraction vary from 46% to 63% (**Fig.4a**). In **S4,** submitted to the Mafragh plume, DIN levels declined to half the value in **S6** with NO_3 fraction forming the essential part of DIN. Indeed, NO_3 fraction represents the dominant form of DIN in the surface waters (**Fig.4a,4b**). The large amounts of DIN appear in the wet season consecutively to continental inputs when the maximum value in Seybouse plume (**S6**) reached 25 µmol.l^{-1} (**Fig.4a**).

Generally, DON concentrations in the Gulf of Annaba are high during all the seasons. Mean values vary from 4 to 11 µmol.l^{-1} (**Fig.4a, 4b**) with a maximum of 25 µmol.l^{-1}. The lowest DIN levels are recorded in the outer stations (**S1**, **S2**, **S3**, **S5**) (**Fig.4b**) reflecting the characteristics of external waters under MAW influence. In these outer stations, NH_4 is certainly originating from the wadis discharges as the latter annual levels varied from 1.5 µmol.l^{-1} to 3 µmol.l^{-1} in the estuarine plume (**S4, S6**)(**Fig.4a, 4b**).

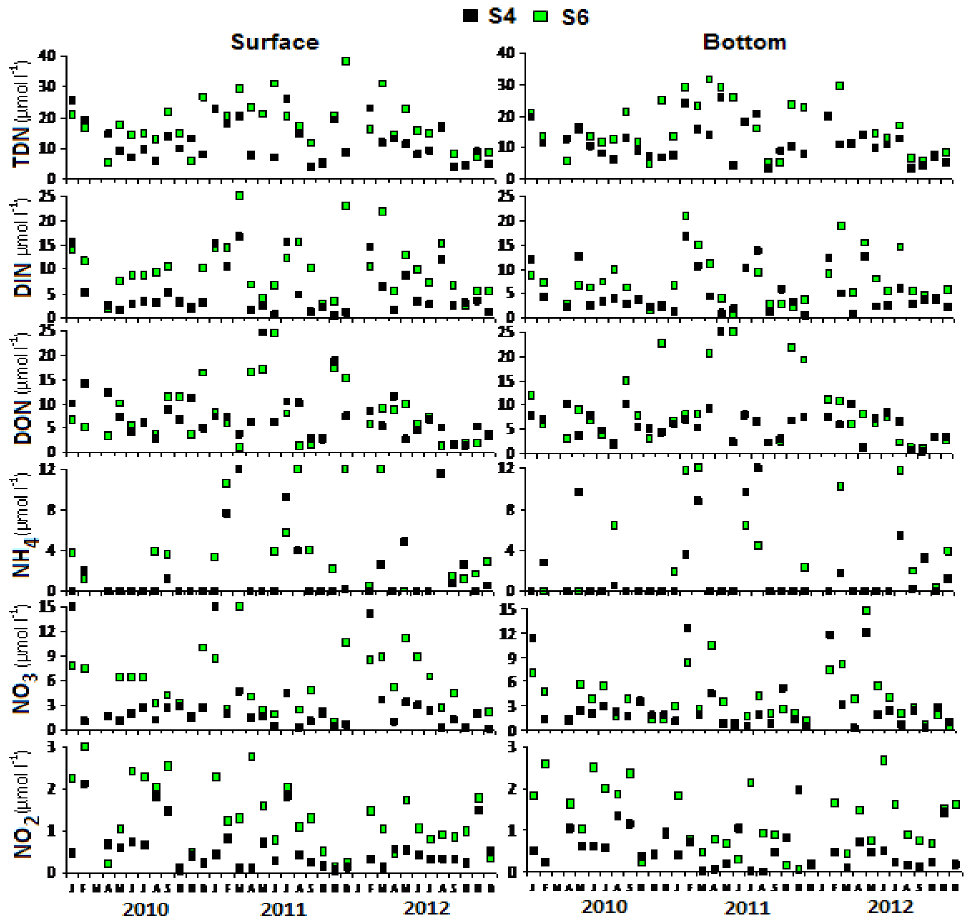

Figure 4a: Variations of nutrient levels in the inner stations **S4** and **S6** (Estuarine plume), (January 2010 to December 2012).

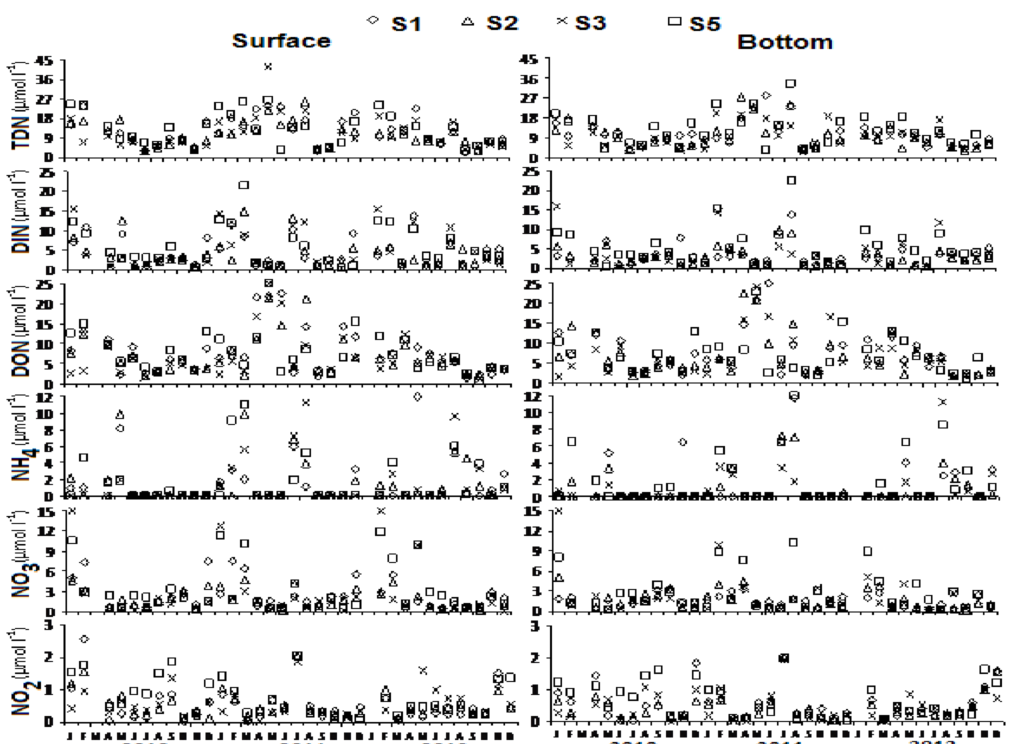

Figure 4b: Variations of nutrient levels in the outer stations **S1**, **S2**, **S3** and **S5.** (January 2010 to December 2012)

The major component of TDP is DIP with 72%, and 28% are in the form of DOP. However, PO_4 shows irregular fluctuations in relation to oxidized nitrogen (**Fig.5a, 5b**). In all the sampled areas of the Gulf (**S1** to **S6**) average surface levels of PO_4 vary from 0.5 to 1.5 µmol.l^{-1} with the maximum 3 µmol.l^{-1} always recorded in the inner stations (**S4**, **S6**) due to continental inputs during the wet season (**Fig.5a**). The outer stations are weakly influenced by continental discharges displaying lower mean values of PO_4 along the year (0.2 to 1.3 µmol.l^{-1}) (**Fig.5b**). As for DIN, bottom levels of PO_4 are close to surface values owing to winter hydrodynamic mixing.

Silicate concentrations vary substantially between the shelf and the frontal waters. Surface water levels of SiO_4 exhibit large differences in spatial distribution between the inner and the outer stations (**Fig.5a,5b**). In the inner stations (**S4**,**S6**), average surface levels are respectively 8 µmol.l^{-1} and 6 µmol.l^{-1} (**Fig.5a**). Indeed, during the wet season, SiO_4 concentrations are very high fluctuating between 6.6 and 12 µmol.l^{-1}. However, in the dry season, the levels decrease to 3.4 and 0.4 µmol.l^{-1}.

Chlorophyll *a* (Chl*a*) and Biogenic Silica (BSi) always occur in low fraction when compared with inorganic matter (**Fig.5a,5b**). Moreover, most of the silicon (>70%) is present in the Gulf as silicate (SiO_4), with BSi presenting a minor percentage (12%) throughout the water column. Chl *a* concentrations range from 0.1 to 7 µg.l^{-1} with the highest records in the S4 and S6 (**Fig.5a**). DIN:PO_4 ratios vary, on average, from 8.5 to 15.6 and SiO_4:DIN ratios fluctuated in all stations around 2 (i.e. From 0.9 to 2.7).

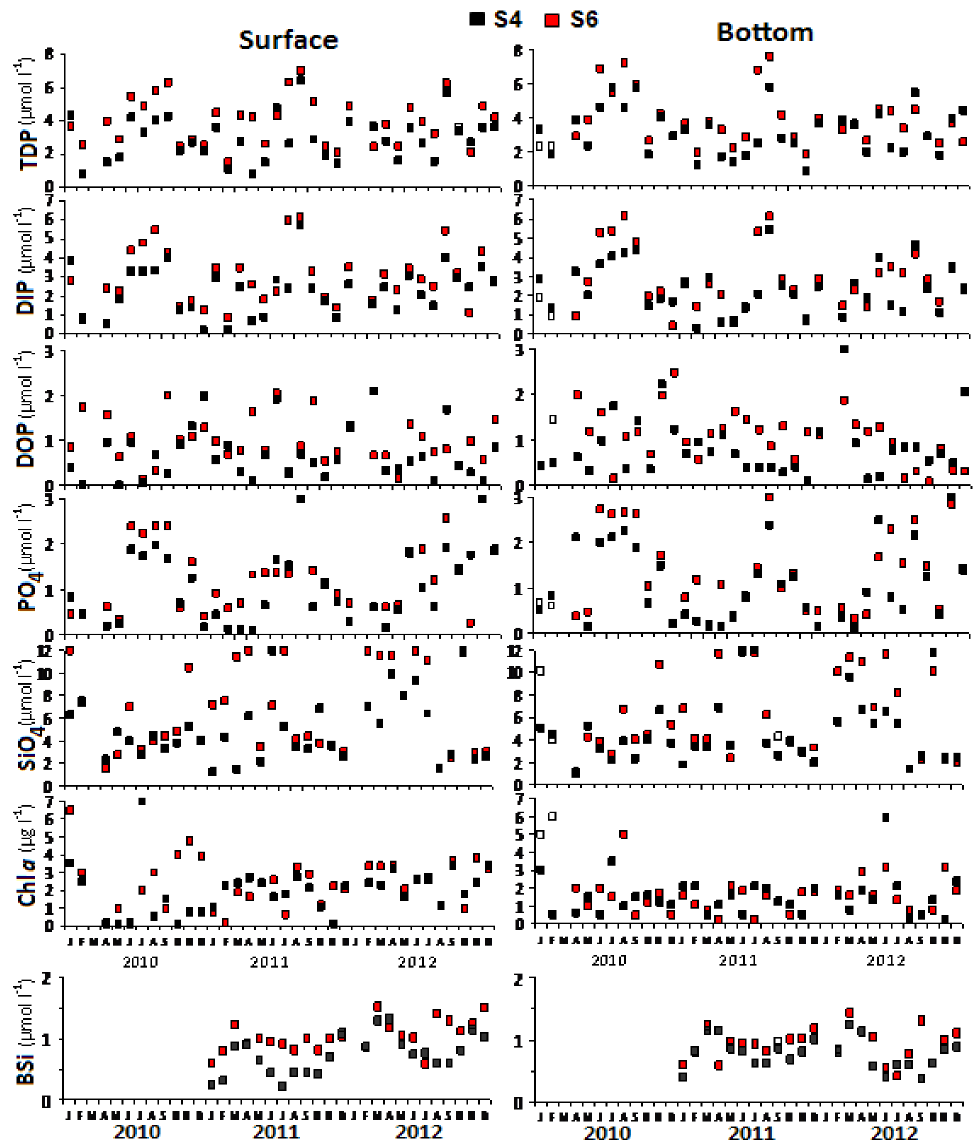

Figure 5a: Variations (January 2010 to December 2012) of nutrient levels and particulate matter in the inner stations **S4** and **S6** (estuarine plume) and of Biogenic Silica (BSi) (2011-2012).

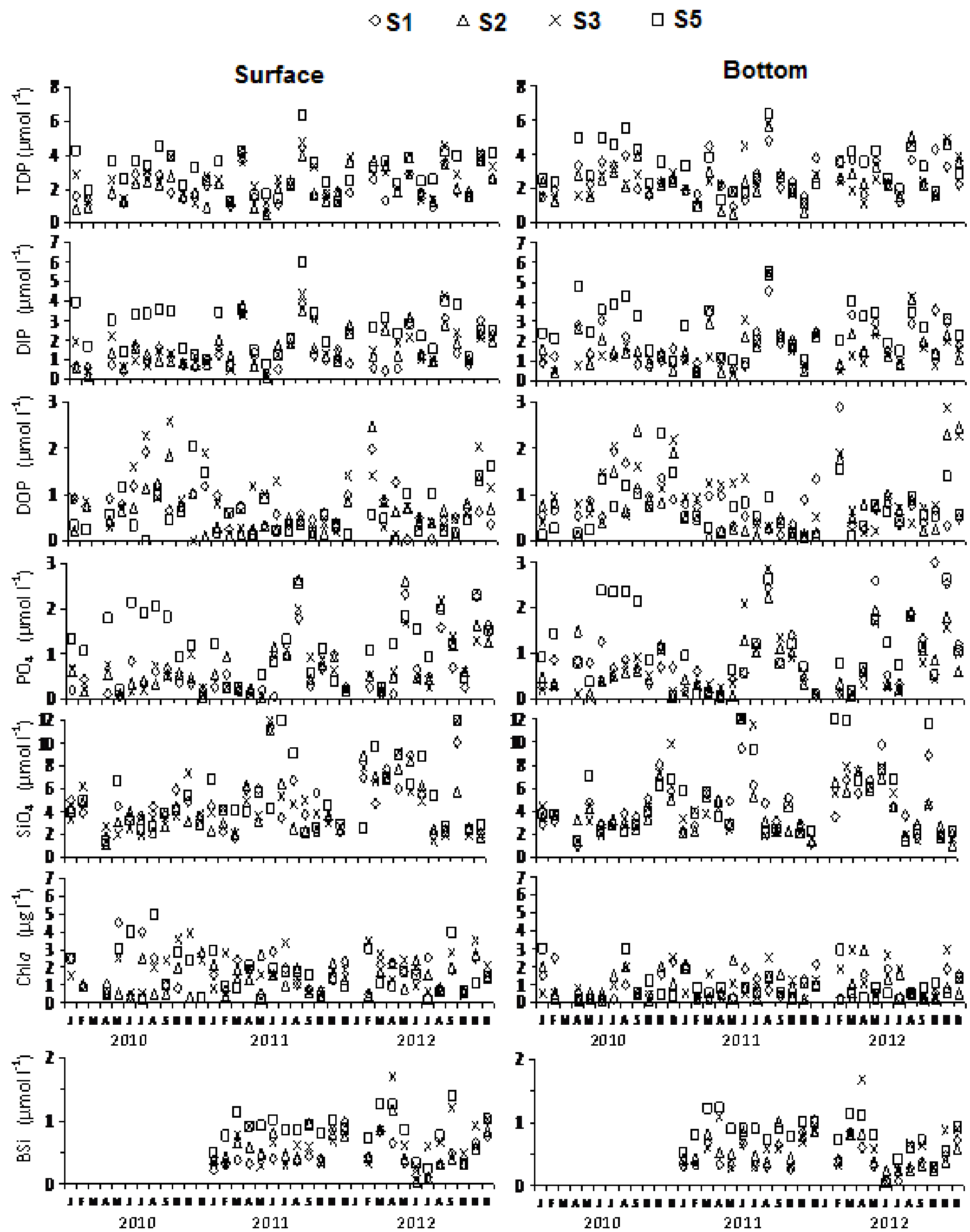

Figure 5b: Variations of nutrient levels and particulate matter in the outer stations **S1**, **S2**, **S3** and **S5** (2010 to December 2012) and of Biogenic Silica (2011-2012).

DISCUSSION

Nitrate is the most abundant fixed nitrogen source in the ocean and varies in concentration depending on habitat. Since the last decades, the coastal areas are under the influence of dramatic escalating nutrient inputs owing to anthropogenic pressure, intensified human urbanization, industrial and agricultural activities [33, 34]. Consequently, anthropogenic eutrophication is the result of an increasing delivery of land-based nutrients considerably enriched with N and P if compared to the supply of Si [35, 36]. Major pollution problems, in Algeria include untreated urban and industrial wastewaters that are discharged untreated directly into the sea [5]. At Annaba, the fertilizer factory is the main hotspot discharging directly into the Gulf waste waters strongly loaded with fertilizers wastes [5, 16] reaching 200 µmol.l^{-1}, 1.8 t.d^{-1} for NH_4 and 30 µmol.l^{-1}, 0.9 t.d^{-1} for PO_4 representing about 300.000 to 400.000

inhabitant-equivalent [37]. Indeed, the local agricultural practices support intensive cultivation consuming enormous quantities of water and fertilizers. Beside, dam effects on biogeochemical transformations are expressed by retaining dissolved inorganic nutrients, producing dissolved organic matter and modulating the balance of the Redfield ratios. In fact, regulation of rivers by dams traps huge masses of sediment and silicon and reduces significantly the flow of silicon to the sea. The imbalance of Si/N, Si/P is a factor of dramatic changes in the coastal ecosystem as well as in the composition of phytoplankton. In the Gulf of Annaba, estuarine excess discharges of DIN compared with SiO_4 lead to the appearance of blooms of harmful *Dinophysis* spp., *Alexandrium* spp. and *Pseudonitzschia multiseries* [23, 24]. Hence, increasing deliveries of land-based nutrients considerably enriched with N and P can lead to high nitrate concentrations and to eutrophication in coastal habitats. If compared to PO_4, the excess of DIN indicates the influence of agricultural waste rather than domestic source. On the other hand, high levels of NH_4, if compared to NO_3, rather suggest a direct impact of domestic wastes on estuarine environment.

To support the increasing human population, production of food and energy has remarkably altered the biogeochemical cycles of nitrogen, phosphorus, carbon and silica [38]. The increased use of nitrogen and phosphorus as fertilizers allowed food production to keep up the pace with the rapid population growth [39]. The amount, forms (dissolved inorganic, organic particulate), and ratios of nutrient discharges in the coastal ecosystems contribute to numerous negative impacts generating human health and ecosystems disorders, loss of habitat and biodiversity, blooms of harmful algae and eutrophication [40, 41, 42, 43, 44]. As a result, freshwater and marine ecosystems can undergo dramatic and severe changes in the fundamental aquatic food chain production.

The growth of diatoms is compromised if the Si:DIN ratio falls below 1:1 [45]. The assessment of the ratios between C, N, P and Si is used to draw inferences on the recycling of nutrients and their possible role as limiting factors for primary production [46]. In addition, gradual changes in the Si:N Redfield ratio are responsible in the severe modifications in the coastal zone productivity, including impacts on regional halieutic resources [42, 47]. Dramatic changes in nutrient loads and composition (Si:N:P ratios) entering the coastal areas can have far reaching effects on the whole coastal ecosystems [48]. Therefore, the actual key topics of coastal research are directed towards changes in the ratios and loadings of N, P, and Si, and the impacts of changing nutrient ratios on phytoplankton composition [49, 50].

In addition to direct urban and industrial wastes, the Gulf of Annaba is under the influence of Seybouse and Mafragh estuaries outputs. It is continuously contaminated through the urban, agricultural, harbor and industrial activities [51, 52]. Recent studies [26] reported that the Gulf of Annaba receives significant urban wastes from Boujemaa effluent of Seybouse (205 and 155 $t.y^{-1}$ respectively, for DIN and PO_4) and from *FERTIAL* wastewaters (950 and 163 $t.y^{-1}$ respectively, for DIN and PO_4) and that DIN specific loadings from the Seybouse outlet range from 77 to 640 $kg.N.km^{-2}\ y^{-1}$. These values can be considered amongst the highest loadings reported in the Mediterranean rivers [5, 15, 22]. Indeed, Seybouse estuary delivers large masses of DON (375 $t.yr^{-1}$) whereas Si-SiO_4 fluxes are about 4865 $t.yr^{-1}$. In contrast, Mafragh wadi crosses a low populated agricultural basin and its outlet shows DIN specific loadings ranging from 34 to 154 $kg.N.km^{-2}.y^{-1}$, although that the P-PO_4 specific loadings vary from 3 to 28 $kg.P.km^{-2}.y^{-1}$. If the levels of PO_4 are more important in the Seybouse outlet waters, Mafragh loadings are paradoxically low varying from 2 to 15 $kg.P.km^{-2}.yr^{-1}$. The low loadings in DIN of Mafragh estuary can be linked to the low populated agricultural basin as well as to the buffering effect of the Mafragh marshland. The major loadings take place during the winter leaching coinciding with the agricultural soil amendment. During the dry season, the wadi outlet deliveries of nutrients are at their minimum [26] as the exchanges from Mafragh to the Gulf are relatively nonexistent.

The estuaries outlets

Water discharge is the main factor affecting matter transfer from land to coastal waters through rivers. In this investigation, it appears that Seybouse waters contributed to over 60% of DIN inputs, characterizing the Seybouse estuary as the major anthropogenic source influencing the chemistry of the Gulf of Annaba. In the same outlet, very high values of NH_4 (51-87 $\mu mol.l^{-1}$) and of PO_4 (2-17 $\mu mol.\ l^{-1}$) are reported in the literature [23, 24]. In this study, Seybouse water contents in NH_4 are very high all along the years, reaching a mean value of 87.5 $\mu mol.\ l^{-1}$. Elsewhere in Ebro River (Spain), NH_4 does not exceed 7% with DIN forms reaching 155 $\mu mol.\ l^{-1}$ [18]. Singularly, Seybouse waters show reduced forms largely dominated (60%) with NH_4 reduced nitrogen form, whereas NO_3 is dominating in the major Mediterranean rivers with values ranging from 20 $\mu mol.l^{-1}$ to 376 $\mu mol.l^{-1}$ [53].

These contrasts are due to the untreated household wastewaters discharged in Seybouse wadi reducing the oxygen levels and allowing the reduced forms to remain stable. It should be emphasized that the fertility of the estuaries of Seybouse and Mafragh wadis is in a higher part due to the NH_4 reserve (48 to 60% of DIN) which preserves the water column from changes in the sediment particularly during the dry period and by the inputs from the continent during the wet period. Oxidized nitrogen is practically exhausted in summer (6.6 µmol. l^{-1} on average) whereas NH_4 remains strongly concentrated in water forming the source of nitrogen for phytoplankton.

Moreover, the dominance of reduced nitrogen is induced by the strongly reducing conditions in the estuary systems due to the anoxia conditions in the water-sediment interface. However, NO_3 concentrations in both estuaries vary greatly with the season (0.2 to 38 µmol.l^{-1}) but remain globally high indicating the enrichment of the estuarine systems. In fact, in the outlet of Seybouse estuary, Ounissi et al. [19] confirmed values ranging from 6.1 to 26.6 µmol.l^{1} with a maximum value reaching 66.6 µmol.l^{-1}. By contrast to Seybouse, Mafragh estuary shows low levels of all nitrogen nutrients and the NH_4 fraction represented only 20%. This estuary appears to be under a weak impact regarding the low levels in NH_4 and PO_4.

Silicon is the seventh most abundant element in the universe. It is a key nutrient element in the ocean required for the growth of diatoms, sponges, radiolarians, silicoflagellates, several species of choanoflagellates, and potentially some picocyanobacteria [54]. The silica cycle is strongly intertwined with the inventory of carbon dioxide in the atmosphere [55]. Recent studies [56, 57, 58] suggest that the silica cycle in coastal zones is highly sensitive to anthropogenic pressure, particularly to damming that decrease concentrations of Dissolved Silicon (DSi) in rivers and estuaries. Consequently, the construction of dams and other water structures has an adverse impact on productivity and diversity of coastal marine waters [59, 60]. When considering Si as a limiting element, which is the case for siliceous phytoplankton species, Si limitation may expand in the Mediterranean rivers and dissolved Si concentrations are reduced to less than half of their pre-dam construction values as it is the case in the Danube and Nile River [61].

The disturbance of water quality entering the Gulf of Annaba exhibit very unbalanced Redfield molar ratios. Depending on the year, SiO_4:DIN molar ratio in Seybouse waters is low along the seasons, fluctuating from 0.9 to 1.6 by contrast to the Mafragh waters showing more elevated values of SiO_4:DIN ratio ranging in average from 3.4 to 5.7. The lowering of SiO_4 in Seybouse discharge (24 µmol. l^{-1} on average) jointly to the high DIN levels lead to SiO_4:DIN lowering. Even if SiO_4 was also lower in the Mafragh estuary, the SiO_4:DIN ratio remains almost balanced as DIN inputs are limited with respect to weak population activities. Hence, the Mafragh estuary constitute an example of SiO_4:DIN molar ratios trend being mainly controlled by human nitrogen inputs rather than estuarine or reservoirs trapping.

Controlling nitrogen inputs in catchments seems to be thus crucial and more primordial compared to challenging Si lowering by dam construction in particular for Mediterranean sub-arid regions [26]. At the opposite of DIN and PO_4 levels, SiO_4 levels show significant decreases in most Mediterranean [15, 22, 62] and European Rivers [61, 63] owing to the reduction of river discharges and to dissolved and biogenic silica retention in dams [59]. Overall, the proportion of 80 % of SiO_4:DIN molar ratios is in all cases below the phytoplankton requirements in Seybouse waters and only 10% cases in the Mafragh outlet. Not only the SiO_4 decreased, but also the levels of DIN increased under large anthropogenic inputs in the lower Seybouse catchment. Hence, both estuaries Mafragh and Seybouse are impoverished in SiO_4 owing to the estuarine buffering area as it is mentioned in the literature [64, 65] as well as to the reservoirs retention at the upper catchments [66, 67, 68].

In this investigation, large amounts of inorganic nutrients are poured into the Gulf of Annaba through Seybouse and Mafragh estuaries with levels reaching respectively DIN:1 304 t.yr^{-1}, 171 t.yr^{-1} of PO_4 and 3 014 t.yr^{-1} of SiO_4 and these values are close to those mentioned in the literature [26]. The DIN specific loadings from Seybouse outlet are high, ranging from 15 to 754 kg N km².y^{-1} according to the year. The P-PO_4 specific loadings are also high (average 25 kg P km².y^{-1}) in contrast to Mafragh outlet where DIN specific loadings are rather low (average 15 to 132 kg N km².y^{-1}). During the wet season, overall loads are estimated at 2 313 t.y^{-1} of SiO_4 introduced by both estuaries in the Gulf. Consequently, Mafragh estuary contributes to about 64% of the SiO_4 transports.

The Gulf

Inorganic nutrients are amongst the most variable components in coastal waters [69]. The estuaries plumes of Seybouse and Mafragh show high levels if compared to the outer waters where nutrient levels declined by 4-fold for DIN, by 5-fold for SiO_4 and by 2-fold for PO_4. Older records reported in the Gulf of Annaba during 1999 [23] and 2007 [24] indicate declining levels by 3-fold for DIN and SiO_4 and by 2-fold for PO_4. On the other hand, this study, showing that large amounts of DON (up to 300 t.yr^{-1}) are introduced into the coastal waters, suggests that this fraction contributes noticeably to the eutrophication the coastal waters of the gulf. Indeed, at the estuaries plumes, peaks of SiO_4 concentrations are related to the decrease in salinity due to the high continental runoff during the rainy season. The highest concentrations occur in **S4** and **S6** (average 12 µmol.l^{-1}). The lowest concentration is undoubtedly induced by the uptake of silicate by the phytoplankton as well as to the slow rate of regeneration of silicate from the sediment.

Multivariate Correspondence Analysis

All the previous observations are reinforced in the findings of the Correspondence Analysis (**Fig.6**).The factorial plan F1 x F2 of the CA provides 87.99 % of the total inertia whereas the first factor (F1) contributes to 58.10 % and the second (F2) to 29.89 %. The first factor is related to the variables DIN and NH_4 associated with Seybouse estuary temporal observations. Seybouse discharges, characterized by high levels of nitrogen nutrients, are opposed to Mafragh waters rather richer in SiO_4. The second factor is related to the levels of SiO_4 distributed in Mafragh estuary. In explaining F2, the contribution of Mafragh estuary is expressed by its high SiO_4 levels.

These features are in opposition to the coastal waters rich in nitrogen nutrients, are rather under the influence of Seybouse estuary strongly enriched with DIN and NH_4. The first factor may represent the anthropogenic effects from the Seybouse estuary a diffusive source heavily loaded in DIN and sensibly lowered in SiO_4 under the particular condition of large damming as it has been reported in cases of contiguous catchments [22]. The second factor may represent the effect of the Mafragh estuary that seems to play a positive role in enriching the adjacent coastal waters.

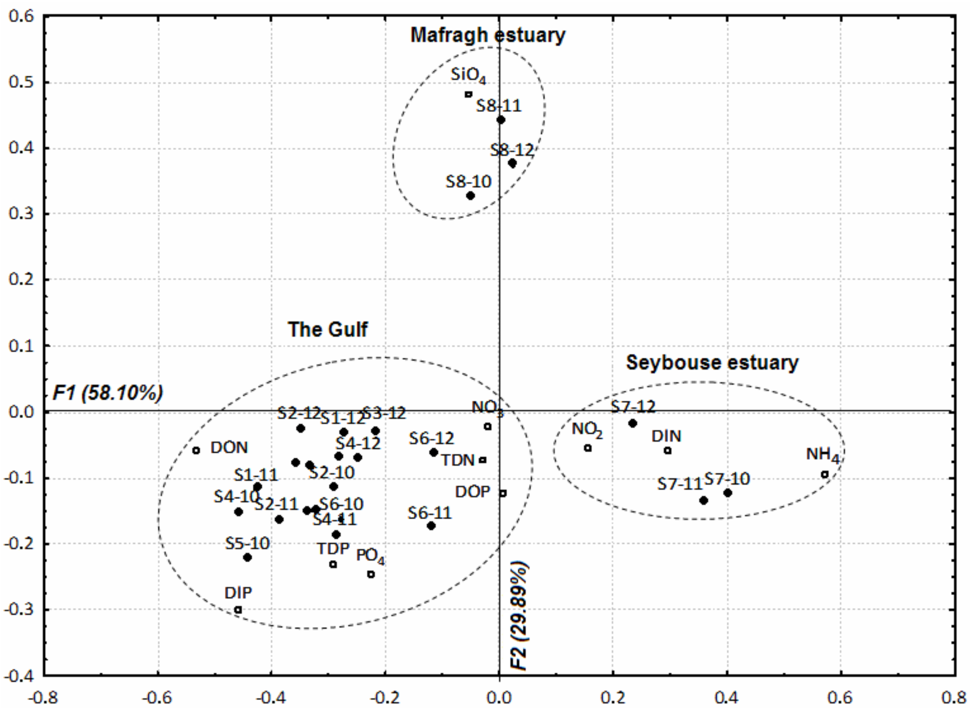

Figure 6: Factorial plan projection F1 x F2 of the correspondence analysis showing three segregated areas. Relating to F1, Seybouse estuary is with high levels in DIN forms in opposition to Mafragh estuary characterized by high levels in SiO_4. Relating to F2, the Gulf stations are in contrast to the estuarine chemical characters.
- Variables: NH_4; NO_2; NO_3; DIN; PO_4; SiO_4; DON; TDN; DOP; DIP; TDP.
- Objects (Stations) in the years 2010; 2011 and 2012:
S7-10; **S7**-11; **S7**-12 Seybouse estuary outlet respectively for the years 2010, 2011 and 2012.
S8-10; **S8**-11; **S8**-12 Mafragh estuary outlet respectively for the years 2010, 2011, 2012.
S1-10; **S1**-11; **S1**-12; **S2**-10; **S2**-11; **S2**-12; **S3**-10; **S3**-11; **S3**-12; **S4**-10; **S4**-11; **S4**-12; **S5**-10; **S5**-11; **S5**-12; **S6**-10; **S6**-11; **S6**-12 Stations of the Gulf.
S1; **S2**; **S3**; **S4**; **S5**; **S6** surveyed in the years 2010, 2011 and 2012: **S1**-10; **S5**-11 behind **S4**-12; **S3**-10 behind **S1**-11, **S3**-11, **S5**-12 behind **S6**-10.

On the other hand, it is obvious that Chlorophyll *a* (Chl*a*) is the most suitable parameter to estimate the trophic state. In the outer Gulf, Chl *a* displays low values (from 0.93 $\mu g.l^{-1}$ to 2.29 $\mu g.l^{-1}$) but relatively high values ($7 \mu g.l^{-1}$) in the inner Gulf. As it may be expected, confined high biomass spots are located near the coast. Nonetheless, the proportion of BSi produced as silicate (12%) is considerably low. Globally estimated in the gulf of Annaba, it represents the fraction of the form of silicon acid produced after the process of dissolution relatively to the total amount silicon in the form of dissolved inorganic acid (SiO_4). The demand for SiO_4 by siliceous phytoplankton has to be balanced by the availability of SiO_4 amounts that represent the sum of the SiO_4 stock and inputs of SiO_4 from various origins (from both estuaries and from the Atlantic water source in the Gulf of Annaba).

Entering the Mediterranean Sea at the Strait of Gibraltar, the Atlantic surface waters show higher concentrations of organic forms, but lower concentrations of mineral forms (PO_4 0.05-0.20 µM; NO_3 1-4 µM; and $Si(OH)_4$ 1-2µM) than the deeper outflowing Mediterranean waters [70]. The atmospheric dust can bring biologically available silica to the sea, but rivers are by far the dominant sources [15]. Rainwater also delivers BSi with values ranging from 0.0 to 6.7 mmol Si $m^{-2}year^{-1}$ near Corsica [71]. Silicon solubility ranges from 0.02% to 1.1% of Saharan dust, which is mainly quartz [72]. However, 10% of silicon may be soluble from feldspar dust [73]. Variability of silica concentrations can be controlled by runoff too, and high values may provoke a dilution effect [42]. River suspended sediment contain great amounts of silicate minerals, but they are insoluble and not available for biological production [15]. Only a small part of the particles contain soluble forms of biogenic particulate silica contribute to about 10-20% of the total silica flux [74, 75, 76, 77]. A recent study [78] suggest that lithogenic material deposited along ocean margins may release considerable BSi into seawater. In the Gulf of Lion in the northwest Mediterranean (2003) the annual average for typical Meditterranean waters the Gulf of Lion is estimated to 0.37 mmol Si m^{-2} d^{-1}[79, 80]. Therefore, it should emphasize that flux advection (i.e. Winter advection) is probably the main processes, setting a limit to the biomass accumulation in the coastal waters.

CONCLUSION

During the wet season, overall loads of SiO_4 are estimated to 2 313 $t.y^{-1}$ introduced by both estuaries into the Gulf. Respectively to this value, Mafragh estuary contributes to about 64% of SiO_4 transfers. Depending on the year of sampling, SiO_4:DIN molar ratio for Seybouse waters is low along the seasons, fluctuating from 0.9 to 1.6 by contrast to the Mafragh waters where SiO_4:DIN ratio is more elevated, ranging in average from 3.4 to 5.8. However, both estuaries seem to be impoverished in SiO_4 owing to the estuarine buffering areas and to the reservoirs retention (Dams) at the upper catchments.

The fertility in the Seybouse and Mafragh estuaries is an integral part of the high NH_4 resource (48 to 60% of DIN). However, both estuaries seem to be impoverished in SiO_4 owing to the buffering estuarine areas and to the reservoirs retention (Dams) at the upper catchments. In the Seybouse discharge, the decrease of SiO_4 values (24 $\mu mol.l^{-1}$ on average), jointly to the high DIN levels, leads to SiO_4:DIN lowering. Even if SiO_4 is also lowered in the Mafragh estuary, the SiO_4:DIN ratio remains almost balanced as DIN inputs are limited because of the very weak human activities in that area as well as around the nearby marshes of El Mekhada.

The lowering flow of Seybouse wadi is not as clear as it is the case in other rivers around the Mediterranean basin. In fact, the release of water from dams and the direct household liquid discharge occult the real flow in the estuary part and directly afterwards in the adjacent coastal waters. During the wet season, 2 313 $t.y^{-1}$ of SiO_4 are introduced into the Gulf of Annaba by both estuaries and Mafragh estuary and contributes to about 64% of SiO_4 transfers. For Seybouse waters, the SiO_4:DIN molar ratio is low all along the seasons fluctuating from 0.9 to 1.6 by contrast to Mafragh waters where SiO4:DIN ratio is higher ranging in average from 3.4 to 5.8.

Noticeably, particulate matter in the Gulf, has always occurred in a low fraction if compared to inorganic matter. Overall, dissolved inorganic nutrient concentrations are low in the dry season and this study shows a general silicon deficiency in the Gulf of Annaba. The impacts of the local anthropogenic activities are affecting significantly the silicon cycle and the biogeochemistry of the coastal zone and the Gulf of Annaba.

The increase in continental weathering due to agricultural expansion and to the recent changes seen in the wadis and the coastal waters related to damming and eutrophication imply that the silica cycle is currently perturbed. The results of this investigation on silica are difficult to evaluate particularly in the temporal evolution since long-term series of values are missing. If compared to the rapid changes of the phosphorus and nitrogen loads, variations in silica are apparently smoother.

Further studies are needed to evaluate the potential impact of the reductions in freshwater inputs on marine ecosystems through the variability of the current dynamics in the Gulf of Annaba. Additional research is also required to determine the wadis inflowing in a week-scale and to assess the levels of loads of nutrients, of dissolved and particulate organic materials in the wadis and the estuarine stations. Investigation on the vertical current velocities, nutrients, plankton biomass and tidal inflow-outflow is therefore necessary for a better understanding of the hydrology of the estuary. It will be a useful tool for an integrated management in flooding control and for a dams-estuary-coastal level assessment system.

Acknowledgments – The authors would like to thank the anonymous referees for helpful suggestions and comments. The work was supported by the Algerian Ministère de l'Enseignement Supérieur et de la Recherche Scientifique (MESRS). The authors declare that they have no conflicts of interest.

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