



# Variability of the dissolved nutrient (N, P, Si) concentrations in the Bay of Annaba in relation to the inputs of the Seybouse and Mafragh estuaries



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## ABSTRACT

Dissolved inorganic nitrogen (DIN), phosphate ( $\text{PO}_4$ ) and silicic acid ( $\text{Si}(\text{OH})_4$ ) loads from the Seybouse and the Mafragh estuaries into the Bay of Annaba, Algeria, were assessed at three stations of the Bay over three years. The Seybouse inputs had high levels of DIN and  $\text{PO}_4$ , in contrast to the Mafragh estuary's near-pristine inputs;  $\text{Si}(\text{OH})_4$  levels were low in both estuaries. The DIN: $\text{PO}_4$  molar ratios were over 30 in most samples and the  $\text{Si}(\text{OH})_4$ :DIN ratio was less than 0.5 in the Seybouse waters, but nearly balanced in the Mafragh. The specific fluxes of Si– $\text{Si}(\text{OH})_4$  ( $400\text{--}540 \text{ kg Si km}^{-2} \text{ yr}^{-1}$ ) were comparable in the two catchments, but those of DIN were several-fold higher in the Seybouse ( $373 \text{ kg N km}^{-2} \text{ yr}^{-1}$ ). The inner Bay affected by the Seybouse inputs had high levels of all nutrients, while the Mafragh plume and the outer marine station were less enriched.

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## 1. Introduction

Coastal zones and their resources are important contributors to economic development and quality life. Their exploitation represents a significant source of income for coastal people, through fisheries, agriculture and tourism. Therefore, their preservation is a first-order priority for stable socio-economic development in the Mediterranean region (Turley, 1999). In oligotrophic seas such as the Mediterranean Sea, nutrient from rivers play a critical role in sustaining the marine productivity, and zones of high productivity are mainly limited to the coastal waters that receive major freshwater inputs (Bosc et al., 2004). For rivers that feed the Mediterranean Sea, Ludwig et al. (2009) reported that fluxes of N and P were strongly enhanced by anthropogenic sources and that their total inputs to the Mediterranean Sea may have increased by a factor >5. In contrast, a decrease in dissolved silica (Si) may be expected. It is strongly controlled by water discharge and also potentially reduced by river damming. Humborg et al. (2000) reported that Si limitation may expand in the Mediterranean Rivers over recent decades, and dissolved Si concentrations have been reduced to less than half their pre-dam construction values in the Danube and Nile Rivers. They also concluded that the dramatic changes in nutrient loads and composition (Si:N:P ratios) entering coastal seas will have far-reaching effects on coastal ecosystems. Turner et al. (1998) described how freshwater and marine ecosystems can un-

dergo fundamental aquatic food web changes as diatom growth is compromised when the Si:DIN ratio falls below 1:1.

Therefore, a key topic of coastal research now centers around changes in the ratios and loading of N, P, and Si and their effects on phytoplankton composition (Béthoux et al., 2002; Cloern, 2001; Howarth and Marino, 2006; Justic et al., 1995). However, the study of river syndromes at a global or regional scale is still limited by the available information (Meybeck, 2003) and impacts of some river syndromes on aquatic resources are already considered as a first priority.

Data on river nutrient loading to the Mediterranean basin are scarce and are missing for many eastern and North African countries, so the general picture is biased (Ibáñez et al., 2008; Ludwig et al., 2009; Milliman, 2007). In Algeria, despite the notable lack of data on nutrient loads from river watersheds to the receiving shelf, there has been no research until now on the distribution of dissolved nutrients in coastal areas in relation to river inputs. For the Bay of Annaba, the few published data are very limited in temporal and spatial scales, and they address only the distribution of the inorganic nitrogen and phosphate in the inner sector of the Bay of Annaba (Frehi et al., 2007; Ounissi and Frehi, 1999) and seasonal fluxes of the same nutrients from the Mafragh estuary (Khélifi-Touhami et al., 2006). The Bay of Annaba receives diffuse inputs from the Seybouse and the Mafragh estuaries in addition to direct urban and industrial wastes. The estuary' watersheds cover approximately  $10,000 \text{ km}^2$  and together house over two million people, for whom intense agricultural practices have become the most important economic activity in the last decade. The population increases and its activities and anthropogenic activity have increased inputs from household waste,

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and a large amount of water is now retained by dams (Ounissi and Bouchareb, 2013) for irrigation. Fertilizer use can also induce changes in the functioning of the adjacent coastal ecosystem. The Seybouse estuary is major contributor of nutrient inputs to the coastal waters. The industrial waste from a large fertilizer factory delivers over  $1 \text{ million m}^3 \text{ d}^{-1}$  of water that is heavily loaded with ammonium and phosphate (Ounissi et al., 2008). Moreover, untreated domestic waste delivers approximately  $0.3 \text{ million m}^3$  of water with heavy ammonium and phosphate loads. Human influences and an irregular hydrological regime are the common features in Mediterranean River systems, which affect both coastal and inland water characteristics.

The objectives of the present study were (1) to estimate nutrient (N, P and Si) fluxes from the Seybouse and Mafragh estuaries and (2) to assess how much that transfer influences the temporal and spatial distribution of nutrient levels and ratios in the Bay of Annaba.

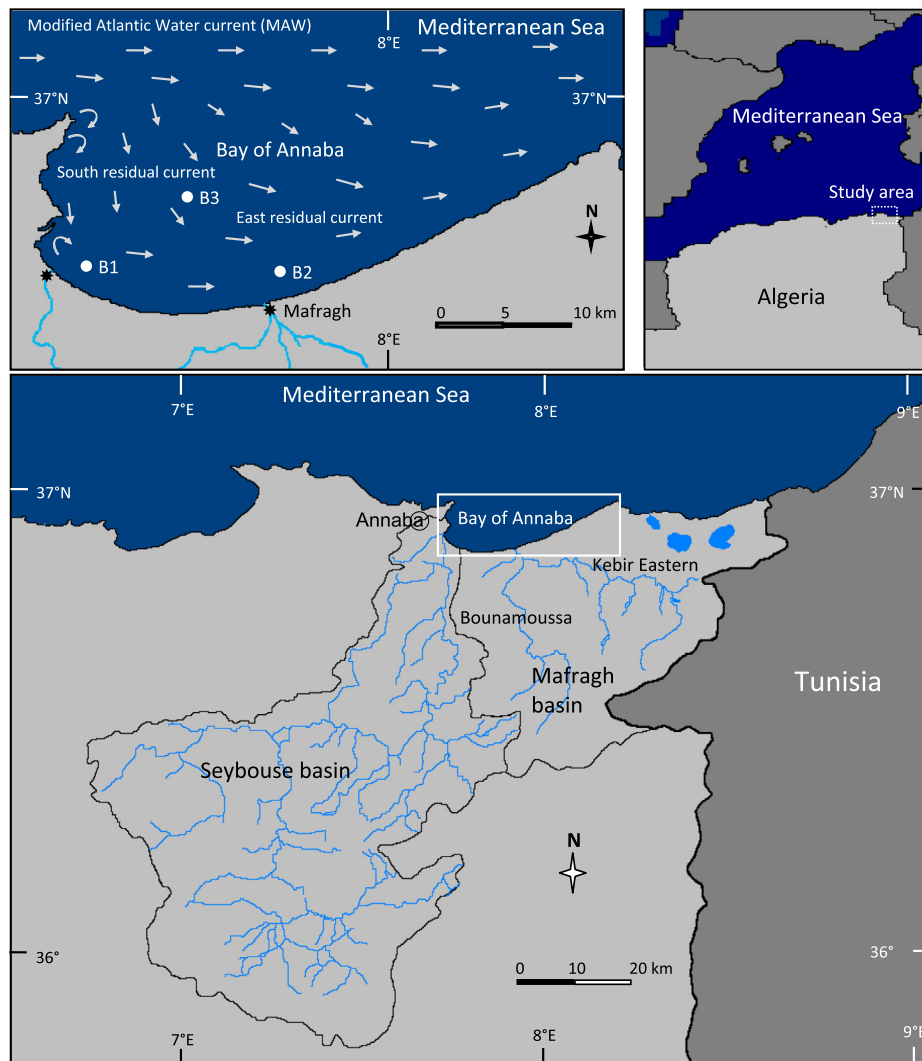
## 2. Sampling sites and methods

### 2.1. Sampling sites

In the Bay of Annaba, the Modified Atlantic Water current (MAW) moves eastward from the marine side (Millot and

Taupier-Letage, 2005) and crosses the shelf of Annaba (Fig. 1), which allows some renewing of the outer neritic waters (Ounissi and Frehi, 1999). However, the inner part of the bay mostly influenced by continental inputs from the Seybouse and the Mafragh estuaries (Fig. 1) and urban waste of the roughly one million people in the city of Annaba and its surrounding villages. Moreover, industrial waste from a single large fertilizer factory deposited over a million  $\text{m}^3 \text{ d}^{-1}$  heavily loaded with nitrogen and phosphorus compounds.

Except during the winter wet season, when rivers discharge freshwater into the bay, the Seybouse and Mafragh Rivers are tidal estuaries, with large seasonal fluctuations in their salt water intrusion. The Mafragh and Seybouse appear as atypical estuaries with the hydrologic cycle comprising river phase, estuarine core phase and lagoonal phase (Khélifi-Touhami et al., 2006). The duration of each phase may strongly vary with the river input and the duration of dry season (Fig. 2). The Mafragh estuary's mouth might be closed from its tidal connection under extended period of dry years. Following periods of high rainfall (winter and in the beginning of spring) and freshwater runoff, the volume of the estuary is entirely discharged into the sea, and the salt wedge is then retreated to the coast in a few days. From the middle spring to the end of autumn, the estuary is dominated by tidal advection, and



**Fig. 1.** Map of the Seybouse and Mafragh rivers' catchments and the adjacent coastal area showing the sampling sites at the estuaries' outlets (•), and the Bay of Annaba (B1; B2 and B3).

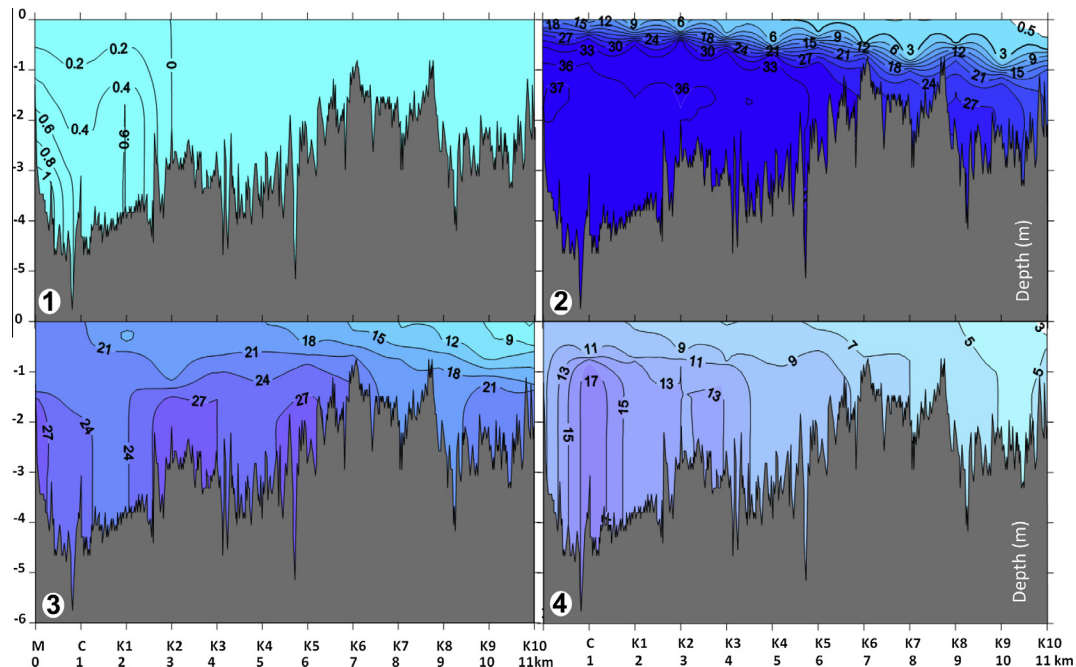


Fig. 2. Salinity profiles (pss) for the Mafragh estuary (Kebir western branch) in 2006, from the mouth (M), the confluence (C) of the two tributaries (Kebir western and Bounamoussa) up to 11 km inland (K1–K11). 1: winter, 2: spring, 3: summer, 4: autumn.

expands in a very stratified system, with two layers (Fig. 2), in which the saltwater layer occupies over 80% of the water column.

The saltwater wedges in the two rivers reach up 8 and 15 km respectively (Khélifi-Touhami et al., 2006).

The population density in the Seybouse basin (6470 km<sup>2</sup>) is approximately 220 inhab.km<sup>-2</sup>, while the Mafragh basin (3200 km<sup>2</sup>) is less populated (80 inhab.km<sup>-2</sup>). Intensive agricultural activity has become the primary land use, and the watersheds are now largely regulated by multiple dams that retain approximately one third (Mafragh) to one half (Seybouse) of the total annual runoff. The Mafragh watershed is, however, distinguished by its large virgin wetlands in the lower reaches, which may act as a buffer for contamination and flood events. In contrast, because of high population density, intensive agriculture and industrialization, the Seybouse is one of the most polluted rivers in Algeria.

Sites for spatial data were selected by purposive sampling using maximum variation technique (Scherrer, 1984). On the shelf of Annaba, three sampling stations were chosen according to the importance of external influences (Fig. 1): the coastal area submitted to the Seybouse estuary plume (Inner Bay, station B1, 6 m depth); the coastal area near the Mafragh estuary (inner Bay, station B2, 19 m depth) and the central Bay far from continental influence and mostly subject to the MAW intrusion (outer water, B3, 40 m depth). To assess the influence of estuarine inputs, the Seybouse and the Mafragh estuaries were sampled at their respective outlet stations.

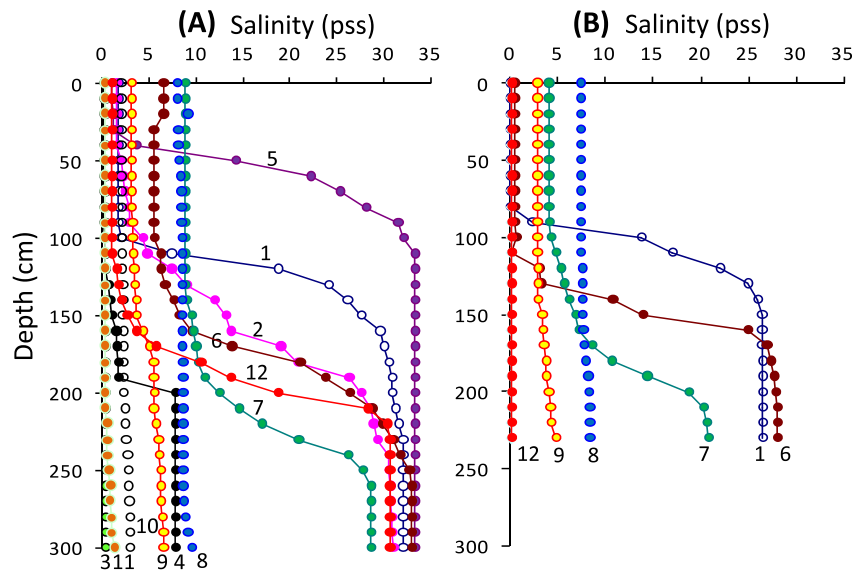
## 2.2. Analytical methods

As we collected water samples, we also measured the flow velocity from the outlet' stations of the Seybouse and Mafragh estuaries with CM-2 current meter, Toho Dentan Co., Ltd., Tokyo. Water salinity and temperature measurements were taken with a multi-parameter probe, WTW 197i. As mentioned by the manufacturer, the precisions of the salinity and the temperature measurements, are respectively  $\pm 0.1$  pss and  $\pm 0.1$  °C. The flow rate (m<sup>3</sup> s<sup>-1</sup>) was calculated by multiplying the water velocity (m s<sup>-1</sup>) by the to-

tal surface area (m<sup>2</sup>) of a transect of the estuary' at the outlet' stations. However, the estimation of the freshwater inputs from highly dynamic and atypical estuarine systems was not easy to carry out. This suggests some explanations. For example, the estuarine part varies with the season from 0 to 7 km in the Seybouse River estuary, and from 0 to 20 km in the Mafragh River estuary (Fig. 3B). If we measure nutrient concentrations and water discharge at 7 km in the Seybouse River estuary, where the salinity is near 0 pss (freshwater), we estimate here what is introduced to the estuary. By the opposite, when we determine water discharge at the mouth, we always measure what is introduced to the sea from the estuary in dry season and from the River in wet season. The problem now is how to estimate the amount of the fresh water discharged, from the estuary, into the sea in such highly dynamic systems. The tide in the estuaries is semidiurnal and microtidal, where the ebb and flood phases duration vary largely. Depending on river flow in particular, the flood phase fluctuates between 0 and 6 h, and the ebb tide one varies between 6 and 24 h (but the discharge may continue for several days because the tide regime is masked by high river flow). The other constraint is the depth of the fresh water layer. We determine at each sampling the periods of the tidal phase, and the fresh water layer as can be seen in Fig. 3A. The measurements of salinity were taken vertically each 10 cm. For example, in May (purple<sup>1</sup> circle), the freshwater layer is about 45 cm; April: 190 cm (black circle); August: 0 cm (blue circle), and so on (Fig. 3A). Having the current velocity, the freshwater layer, the ebb tide phase duration, we can determine the estuarine inputs.

Two liters of water from the middle of the flow were collected for nutrient analysis. Surface water samples were taken in the estuaries monthly from January 2007 to December 2009 and from March 2007 to December 2009 in the Bay of Annaba. The Seybouse estuary was only sampled twice in the years 2008 and 2009. Due to bad weather in the Bay of Annaba, we were unable to collect several samples: May 2007; March; September and November 2008;

<sup>1</sup> For interpretation of color in Fig. 3, the reader is referred to the web version of this article.



**Fig. 3.** Monthly vertical profiles of salinity at the outlet (A) and at 11 km from the outlet (B) of the Mafragh estuary (kebir Eastern branch), during the year 2007. The circles 1 to 12 correspond successively to the salinity profiles of January to December. In graphic B, values of 2, 3, 4, 5, 10 and 11 are near zero, and are superimposed on the depth axis.

and September 2009. In addition to surface water sampling in the Bay of Annaba, bottom waters were sampled using Niskin bottle. Water samples for nutrient analyses were frozen in polyethylene bottles and processed within 2 days of collection. In the laboratory, after filtration of the sample through a Whatman GF/C glass filter (0.5  $\mu\text{m}$  porosity), all nutrient (phosphate:  $\text{PO}_4$ ; ammonium:  $\text{NH}_4$ ; nitrate:  $\text{NO}_3$ ; nitrite:  $\text{NO}_2$ ; silicic acid:  $\text{Si}(\text{OH})_4$ ) concentrations were determined by means of the standard colorimetric methods described by Parsons et al. (1989). Their precisions are:  $\pm 3\%$  ( $\text{PO}_4$ ), 5% ( $\text{NH}_4$ ), 3% ( $\text{NO}_3$ ), 2.5% ( $\text{NO}_2$ ), 2.5% ( $\text{Si}(\text{OH})_4$ ). The instantaneous flux of nutrients was calculated by multiplying their levels by the estuary flow. The annual loads for nutrients were estimated using the method of average instantaneous loads (Preston et al., 1989):

$$F = K \sum_{i=1}^n \frac{C_i Q_i}{n}$$

where  $F$  is the annual load (tons/year or  $\text{t yr}^{-1}$ ),  $C_i$  is the concentration of nutrients ( $\mu\text{mol l}^{-1}$  or  $\mu\text{M}$  converted to  $\text{kg m}^{-3}$ ),  $Q_i$  is the concomitant instantaneous flow ( $\text{m}^3 \text{s}^{-1}$  converted to  $\text{m}^3 \text{day}^{-1}$ ),  $n$  is the number of days with concentration and flow data and  $K$  is the conversion factor to consider the period (365 days) and unit of estimation.

### 2.3. Statistical analysis

Even though purposive sampling offers a substantial amount of information relative to the sampling effort, all estimators are subject to significant bias including correlation, mean, variance, etc. (Scherrer, 1984). In fact, the stations have been placed to collect data at strategic points (outlets and their marine plumes and the outer marine station affected by the MAW current) or to find possible gradients.

The intentional placement of the stations may be responsible for correlations between nutrients and spatiotemporal variability, but these factors have not been considered in this work. However, data issued from purposive sampling can reveal interesting findings when used in multivariate factorial analyses, especially in environmental diagnosis and to find trends along spatial gradient of the variables (Scherrer, 1984). A correspondence analysis (CA) multivariate technique was then used to determine any possible

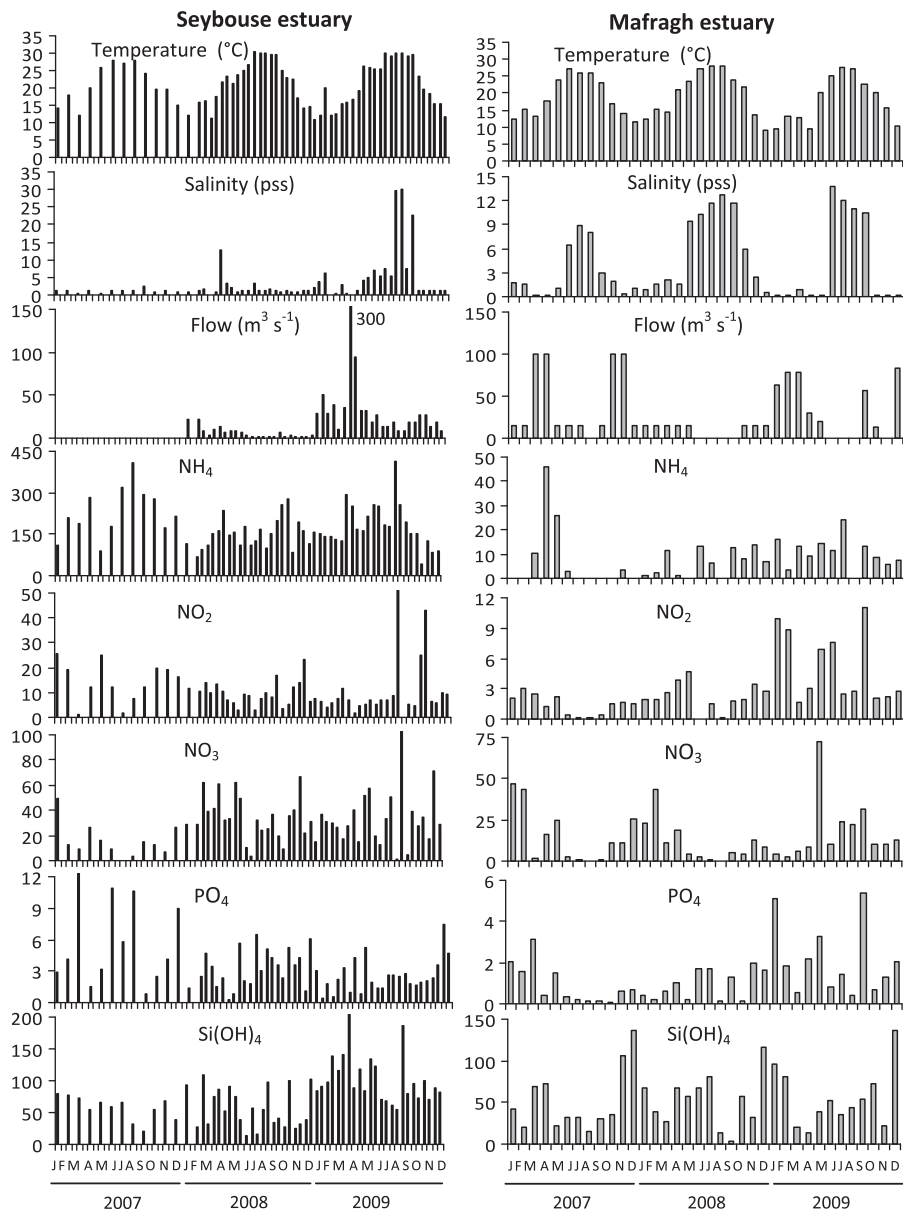
co-variation between inorganic nutrients and their ratios, both in the estuaries' outlets and at the coastal stations, during the three years of surveys. The CA has several advantages compared to multivariate techniques such as principal component analysis (PCA), and it is more appropriate for the data we collected. Presenting the variables and objects together in a biplot graphic, facilitates the interpretation of the cloud points and their associations. In addition, the CA is a double principal component analysis on the variables (columns) and objects (rows) and also compares rows or columns using the Chi-square distance, which offers a superior method of weighting the individual data. In addition, the data do not need to be normalized, a procedure that can distort reality as it does for PCA (Dervin, 1988). The statistical software Statistica, 2008 was used to perform the CA. The contingency table analyzed with CA is a matrix of the annual averages of 8 nutrient levels and ratios (variables) observed on 15 spatiotemporal situations (objects) representing the two outlets and three coastal stations over three years of survey (2007–2009).

## 3. Results

### 3.1. Hydrology and nutrient variability and fluxes at the estuaries' outlets

The hydrological parameters recorded in the two estuaries are given in Fig. 4. The estuarine water flow at the respective outlets varied according to the precipitation, especially for the Seybouse estuary, where discharges in 2009 were 6-fold higher than those of 2008 (Fig. 4). Because of the large marshland supplying the Mafragh estuary, discharges varied less and seem to be more important than those of Seybouse (Fig. 4). In the Mafragh the inter-annual variability was mitigated, and did not exceed 4-fold because the surrounding wetlands regulate flow. As seen in Fig. 4, the minimum flow was recorded in 2008 because of the low rainfall, as it was for the Seybouse basin. The water temperature varied in the same range in both estuaries, but the annual average value of Seybouse waters was significantly higher because of the amount of wastewater from human population.

In the outlets of the estuaries, the salinity is controlled by river inputs and to a lesser degree by tidal intrusion. In the wet period which extends approximately from November to April, continental



**Fig. 4.** Seasonal variations in temperature, salinity, flow and nutrient levels ( $\mu\text{M}$ ) in the Seybouse and Mafragh estuaries, January 2007–December 2009. Note that there are no flow measurements for the Seybouse estuary in 2007.

inputs dominated the entire estuary, driving the salt wedge back towards the sea. Salinity values then decreased to between 0.5 and 1 pss (Fig. 2a and b). During the dry periods in summer and autumn, marine intrusion dominated and increased the salinity over the entire estuarine layer. Therefore, the observed bottom salinities (not represented here) may be comparable to those of the adjacent shoreline, and the surface salinity ranged between 10 and 30 pss. In the spring and summer, the estuaries were marked by variable salinity depending on the tidal phase. During this period, the surface values fluctuated at some units, reflecting large marine intrusions (Fig. 4). During late summer and autumn, the marine connection of the Mafragh estuary was closed and it appeared to function as a non-tidal lagoon. There, the surface salinity increased to a maximum of 6–14 pss, depending on the historical freshwater inputs (Fig. 4).

The waters from the mouth of the Seybouse were highly charged with dissolved nitrogen forms ( $\text{DIN} = \text{NH}_4 + \text{NO}_2 + \text{NO}_3$ ) and  $\text{PO}_4$ , and the values were higher than any from the Mafragh

estuary (Fig. 4). The dominant character of the Seybouse was its high  $\text{NH}_4$  levels which reached an average of 200–260  $\mu\text{M}$  depending on the year; this represents more than 20 times the levels recorded in the outlet of the Mafragh. The oxidized forms of nitrogen, as  $\text{NO}_3$  plus  $\text{NO}_2$ , always occurred in a low fraction compared to the  $\text{NH}_4$ , which represented more than 80% of DIN. In contrast, in the Mafragh outlet, the oxidized form of nitrogen accounted for 60%. The Seybouse estuary also had high levels of  $\text{PO}_4$ , with an average value of 2.5–6  $\mu\text{M}$ , and the maximum was recorded in the year 2007. Again, the  $\text{PO}_4$  enrichment of the Seybouse waters relative to the Mafragh was several-fold (Fig. 4). The average level in the Mafragh ranged from 1 to 2.5  $\mu\text{M}$ , and the maximum was found in the unusually wet year of 2009.

The  $\text{Si(OH)}_4$  levels, unlike those of DIN forms or  $\text{PO}_4$ , were low in both estuaries, particularly in the dry years of 2007 and 2008, when the average values decreased to 50  $\mu\text{M}$  (Fig. 4). In the exceptionally rainy year of 2009, as seen in Fig. 4, the  $\text{Si(OH)}_4$  levels in-

creased to 100  $\mu\text{M}$  and 56  $\mu\text{M}$  in the Seybouse and Mafragh outlets, respectively.

Because the estuaries buffer nutrient dynamics, the seasonal variations in the outlets were masked. Average levels in the wet period were slightly higher than those of the dry season, particularly in the Seybouse. However, the levels of  $\text{NO}_3$  and  $\text{Si}(\text{OH})_4$  increase by 20–40% in the wet period compared to the dry ones. At the Seybouse outlet,  $\text{NH}_4$  levels were always high, but paradoxically increased by 45% in the dry season. This trend may indicate that  $\text{NH}_4$  is largely from urban inputs.

As shown in Fig. 5, the estuaries released waters with very imbalanced Redfield ratios ( $\text{DIN}:\text{PO}_4$  and  $\text{Si}(\text{OH})_4:\text{DIN}$ ). The disturbance is clearer for the Seybouse estuary, where  $\text{DIN}:\text{PO}_4$  reached an average of 92–135 and  $\text{Si}(\text{OH})_4:\text{DIN}$  did not pass 0.5 (Fig. 5). Not only did nitrogen inputs dominate in the mouth of Seybouse, but there was also a large decrease of  $\text{Si}(\text{OH})_4$  in the upper catchment, which was likely responsible for the sharp decrease in the  $\text{Si}(\text{OH})_4:\text{DIN}$  ratio or the increase of  $\text{DIN}:\text{PO}_4$ . Despite the relative high  $\text{DIN}:\text{PO}_4$  ratio (20.8) in the Mafragh estuary, the  $\text{Si}(\text{OH})_4:\text{DIN}$  appears to be more balanced, its average varying between 2 and 13 (Fig. 5). For both estuaries, all of these ratios were more disturbed in the dry season, when  $\text{Si}(\text{OH})_4$  levels decreased as  $\text{NID}$  and  $\text{PO}_4$  increased.

Nutrient fluxes from the estuaries were highly variable between years, depending principally on river flow (Table 1). The Seybouse estuary introduced large amounts of all nutrients compared to the Mafragh estuary; it carried twice the oxidized nitrogen and  $\text{Si}-\text{Si}(\text{OH})_4$  and more than 20 times the  $\text{N}-\text{NH}_4$ . However, the two estuaries input comparable masses of  $\text{P}-\text{PO}_4$ . Only the  $\text{Si}-\text{Si}(\text{OH})_4$  fluxes were higher in the Mafragh estuary compared to the Seybouse, and only for the dry year of 2008. The Seybouse estuary delivered considerable fluxes of  $\text{DIN}$  in the heavy rainfall year of 2009, of which 84% were in the form of  $\text{N}-\text{NH}_4$ . In contrast, the Mafragh estuary delivered less  $\text{DIN}$ , with a high fraction of oxidized forms as seen in Table 1.

In addition, large amounts of  $\text{Si}-\text{Si}(\text{OH})_4$  were loaded from the estuaries in 2009 in their respective high flows. The maximum specific loading of  $\text{DIN}$  was on the order of  $700 \text{ kg N km}^{-2} \text{ yr}^{-1}$  in the Seybouse outlet and only approximately  $150 \text{ kg N km}^{-2} \text{ yr}^{-1}$  in the Mafragh. However,  $\text{Si}-\text{Si}(\text{OH})_4$  loading of the two watersheds was remarkably comparable in wet years (approximately  $750 \text{ kg N km}^{-2} \text{ yr}^{-1}$ ) and within several tens  $\text{kg N km}^{-2} \text{ yr}^{-1}$  in dry years (Table 1). The  $\text{P}-\text{PO}_4$  specific loadings were found important, ranging from 1 to  $15 \text{ kg N km}^{-2} \text{ yr}^{-1}$  according to the year. Most of these loadings occurred in winter coinciding with agricultural soil amendment. Because they were almost closed, the outlets delivered fewer nutrients in the rest of the year. In addition to the high masses introduced to the bay via Seybouse, the loading ratios

$\text{DIN}:\text{PO}_4$  and  $\text{Si}(\text{OH})_4:\text{DIN}$ , were also unbalanced. The  $\text{DIN}:\text{PO}_4$  ratio was above 30 and the  $\text{Si}(\text{OH})_4:\text{DIN}$  was below 1.

### 3.2. Hydrology and nutrient variability in the bay

The temperature ranged between  $12^\circ\text{C}$  and  $28^\circ\text{C}$ , with a minimum in February, a maximum in August and an average value of  $19\text{--}21^\circ\text{C}$ , depending on the station. Through the seasons and years, the surface salinity fluctuated between 23 and 37.9 pss (Fig. 6). The lowest salinity values were recorded at the inner station B1, located at the Seybouse plume, and their averages varied in the range of 32–36.4 pss. The other inner station, B2 of the Mafragh plume, showed comparable but elevated surface values ranging from 34 to 36.8 pss (Fig. 6). Surface salinity values increased to 36.5–37 pss in the outer coastal waters (station B3) but remain stable throughout the seasons. Here, freshwater influences were so limited that the salinity deviation did not exceed 0.5 pss (Fig. 6), a value that reflects the major hydrological features of the Modified Atlantic Water (MAW) that prevails the Bay of Annaba. The estuarine influence on coastal waters was also expressed by the stratification in the shallower waters of station B1 and to a lesser extent in station B2. These influences did not reach the outer waters of station B3 because of thorough mixing and a constant salinity through the entire water layer (Fig. 6). Instead, this area is under the influence of external waters via the residual current of MAW penetrating the Bay.

Station B1 directly reflected to the Seybouse inputs and showed the highest levels in all nutrients, as shown in Fig. 6. Through the years the  $\text{DIN}$  surface levels remain almost unchanged, fluctuating around  $10 \mu\text{M}$  in the Seybouse plume, and  $\text{NH}_4$  is the main fraction of  $\text{DIN}$ . Only the rainy year of 2009 showed significantly elevated values (Fig. 6). Station B2 corresponds to the Mafragh plume, and the  $\text{DIN}$  levels were half those of station B1, with the  $\text{NH}_4$  proportion still forming the essential part of  $\text{DIN}$ . Station B3 had the least  $\text{DIN}$ , which reflects the characteristics of external waters. The  $\text{NH}_4$  fraction was the dominant form within  $\text{DIN}$  of surface waters (Fig. 6). Large amounts in  $\text{DIN}$  appeared in winter after the continental inputs (Fig. 6). At times the  $\text{DIN}$  levels were lower, especially in the surface waters at station B3, but in no season were they depleted. Even if  $\text{NO}_3$  ions are known to originate from river discharges, their levels in the Bay throughout the year are only in the order of  $1 \mu\text{M}$  in station B2 and B3 and  $3 \mu\text{M}$  in the Seybouse plume (B1). Dilution effects undoubtedly lowered the levels of this nutrient because its level in the Seybouse inputs was about  $30 \mu\text{M}$ . Because of the high hydrodynamic forcing that induces thorough mixing in winter and spring, the water column in the shallower waters of station B1 showed the same  $\text{DIN}$  levels. The other deeper

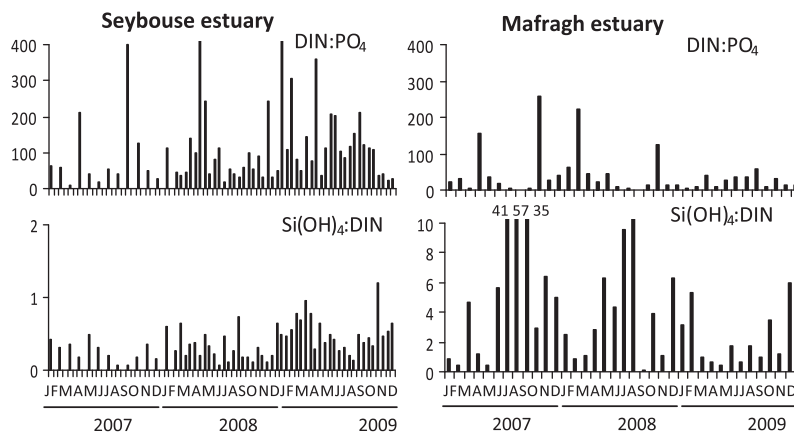


Fig. 5. Variations in  $\text{DIN}:\text{PO}_4$  and  $\text{Si}(\text{OH})_4:\text{DIN}$  ratios in the Seybouse and Mafragh estuaries during the period January 2007–December 2009.



the Bay (Fig. 6). As for DIN, the levels of  $\text{PO}_4$  at the bottom were comparable to surface values because of winter hydrodynamic mixing. There were however, some perceptible differences between the Mafragh plume and the outer station (Fig. 6).

Similar to the DIN levels,  $\text{Si}(\text{OH})_4$  at the surface followed a clear spatial distribution with large differences between the station plumes and the outer station (Fig. 6). In the plumes of the estuaries, average surface levels were on the order of  $6 \mu\text{M}$  for the Seybouse and  $4 \mu\text{M}$  for the Mafragh. On the surface of the outer waters at station B3,  $\text{Si}(\text{OH})_4$  increased to  $2 \mu\text{M}$  but fluctuated greatly throughout the years, between 1 and  $9 \mu\text{M}$  (Fig. 6). The bottom levels were always comparable in the plume stations, but were significantly different from the deeper station in the outer waters.

The Redfield ratios were generally disturbed in all stations in both the surface and bottom waters (Fig. 7). Depending on the station and the year, the DIN: $\text{PO}_4$  ratios were below 10 in 50–70% of samples and the  $\text{Si}(\text{OH})_4$ :DIN ratios were below 1 in 50–70% of samples (Fig. 7). In all stations, the DIN: $\text{PO}_4$  average ratios varied between 2.3 and 11.6, except at the station B1 in 2007 which recorded a ratio of 30. Even though the average values of the  $\text{Si}(\text{OH})_4$ :DIN ratios fluctuated around 1 (0.86–1.6) in all of the stations, they were also imbalanced and below 1 for 50–70% of samples (Fig. 7).

#### 4. Discussion

The objective of this work was to estimate the inorganic nutrient (N, P and Si) fluxes from Seybouse and Mafragh estuaries and to evaluate how much the transfer influenced the distribution of nutrient levels in the Bay of Annaba. Very little is known about the hydrology and chemistry of the Algerian estuaries and their adjacent coasts. Though there is some information about the seasonal nutrient (DIN and  $\text{PO}_4$ ) inputs from the Mafragh estuary (Khélifi-Touhami et al., 2006) and the works of Ounissi and Frehi (1999) and Frehi et al. (2007) describe the DIN and  $\text{PO}_4$  observed in the inner part of the Bay of Annaba, information on the Bay hydrology is still lacking.

##### 4.1. The estuaries

The two estuaries introduced large amounts of inorganic nutrients into the Annaba Bay: DIN:  $2675 \text{ t yr}^{-1}$ ; P- $\text{PO}_4$   $105 \text{ t yr}^{-1}$  and Si- $\text{Si}(\text{OH})_4$ :  $4347 \text{ t yr}^{-1}$ . The Seybouse alone contributed over 80% in of the DIN. For  $\text{Si}(\text{OH})_4$ , the two estuaries supplied comparable fluxes, which originated from land weathering. According to this study, the Seybouse appears to be the major anthropogenic source

influencing the chemistry of the Bay of Annaba. In the plume of Seybouse, Frehi et al. (2007) and Ounissi and Frehi (1999) reported very high values in  $\text{NH}_4$  ( $24\text{--}40 \mu\text{M}$ ) and  $\text{PO}_4$  ( $2\text{--}17 \mu\text{M}$ ). The Seybouse waters were heavily charged with  $\text{NH}_4$  throughout the year, with an average as high as  $200 \mu\text{M}$ . The Seybouse waters were strongly dominated by the  $\text{NH}_4$  form of reduced nitrogen (80%), which is unusual, compared to the major Mediterranean Rivers where  $\text{NO}_3$  dominates. For Mediterranean Rivers, the EEA (2007) reports elevated values of  $\text{NO}_3$  ranging from 20 to  $376 \mu\text{M}$ , and in the Ebro River,  $\text{NH}_4$  did not exceed 7% of the DIN forms ( $155 \mu\text{M}$ ) according to Ibáñez et al. (2008). These contrasts may be related to the untreated household wastewaters that are released into the Seybouse river-estuary. Additionally, the high  $\text{PO}_4$  levels ( $4 \mu\text{M}$ ) characterizing the river suggest a strong influence of domestic wastewater. The implementation of European water quality legislation has had a direct impact on the Mediterranean coastal areas.  $\text{PO}_4$  levels decreased 6-fold between the late 1980s and 2002 (Torrecilla et al., 2005) for the Ebro River. In addition, the Po River (Cozzi and Giani, 2011), the Rhone River (Diaz et al., 2008), the Têt River (Garcia-Esteves et al., 2007), the Gediz River (Suzal et al., 2008) and several Greek Rivers such as the Pinios (Bellos et al., 2004) and Axios River (Nikolaïdis et al., 2009) all saw significant reductions in nutrient loads.

By contrast to the Seybouse estuary, the Mafragh estuary had low levels of all nutrients, and within the nitrogen pool, the  $\text{NH}_4$  fraction represented only 30%. However both estuaries seem to be impoverished in  $\text{Si}(\text{OH})_4$  owing to the estuarine buffering (Canton et al., 2012; Hallas and Huettel, 2013) and to the reservoirs retention (Avilés and Niell, 2007; Humborg et al., 2006; Meybeck and Vörösmarty, 2005) in the upper catchments. Before reaching the coast, riverine nutrients passes through estuaries which act as filters for material derived from land (Canton et al., 2012; Hallas and Huettel, 2013). The disturbance in the quality of water entering the Bay was also expressed in unbalanced Redfield molar ratios. The  $\text{Si}(\text{OH})_4$ :DIN molar ratio for Seybouse waters was low in all seasons, and fluctuated depending on the year from 0.25 to 0.5. In contrast, the Mafragh waters had elevated  $\text{Si}(\text{OH})_4$ :DIN ratios, ranging on average from 2.2 to 13.4. The lesser amount of  $\text{Si}(\text{OH})_4$  in the Seybouse discharge ( $73 \mu\text{M}$  in average) along with the high DIN levels led to the low  $\text{Si}(\text{OH})_4$ :DIN ratio. Even though  $\text{SiO}_4$  was also low in the Mafragh estuary, the  $\text{Si}(\text{OH})_4$ :DIN ratio was unbalanced because the anthropogenic inputs was also low. In this case, the Mafragh estuary may be a good example of  $\text{Si}(\text{OH})_4$ :DIN molar ratio trends being controlled by human nitrogen inputs rather than retention in estuaries or reservoirs. Controlling the nitrogen inputs in the catchments therefore seems to be a higher priority than trying to increase Si by lessening dam

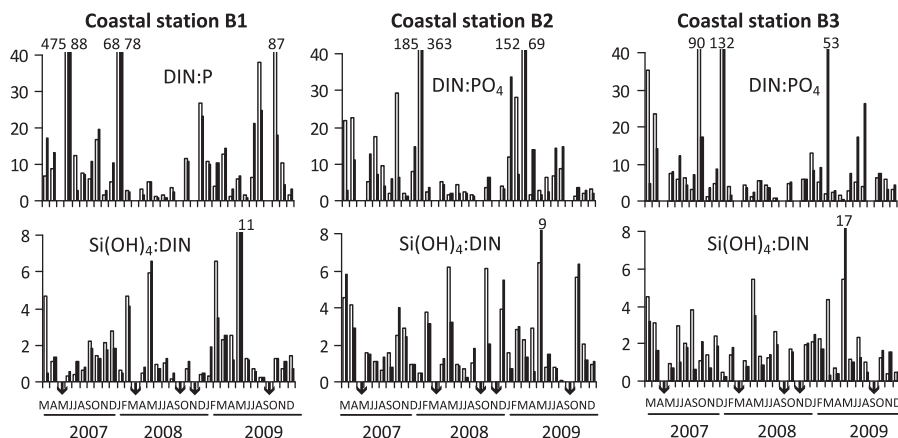


Fig. 7. Variation in DIN: $\text{PO}_4$  and  $\text{Si}(\text{OH})_4$ :DIN ratios in the coastal stations (B1; B2; B3) of the Bay of Annaba during the period March 2007–December 2009. □ Surface; ■ bottom; ▼: not sampled.

construction, in particular for Mediterranean sub-arid regions. As opposed to DIN and  $\text{PO}_4$  levels,  $\text{Si}(\text{OH})_4$  decreases significantly in most Mediterranean (Billen and Garnier, 2007; Ludwig et al., 2009; Ounissi and Bouchareb, 2013) and European Rivers (Conley, 2002; Humborg et al., 2000) owing to the reduction of river discharge and to the retention of dissolved and biogenic silica retention by dams (Conley et al., 2000). Additionally, the  $\text{Si}(\text{OH})_4$ :DIN was always below the phytoplankton requirements in Seybouse waters and about 30% of samples from the Mafragh outlet. Not only did the  $\text{Si}(\text{OH})_4$  decrease, but the levels of DIN increased under large anthropogenic inputs from the lower Seybouse catchment. The high and balanced  $\text{Si}(\text{OH})_4$ :DIN values in the Mafragh may be related to its large marshland water supply, despite some human population and activity over the catchment. In addition, the  $\text{NID}:\text{PO}_4$  molar ratio was also unbalanced in all of the Seybouse samples, with average values varying in the range of 90–135 according to the year. The excess of DIN compared to  $\text{PO}_4$  seems to indicate an influence of agricultural waste rather than domestic point source inputs. On the other hand, the much higher level of  $\text{NH}_4$  compared to  $\text{NO}_3$  rather suggests that domestic wastes do impact this estuarine environment. In the Mafragh outlet, the  $\text{DIN}:\text{PO}_4$  molar ratios were below the phytoplankton needs about half the time, and the annual average values ranged from 24 to 50. Because of the dominance of  $\text{NO}_3$  jointly and low levels of  $\text{PO}_4$ , the Mafragh waters are most likely influenced most by agricultural fertilizers.

The DIN specific loadings from the Seybouse outlet were high, ranging from 77 to  $640 \text{ kg N km}^{-2} \text{ yr}^{-1}$  depending on the year. These amounts may be considered among the highest in Mediterranean Rivers (EEA, 2007; Ludwig et al., 2009; Ounissi and Bouchareb, 2013). In contrast to Mafragh outlet where DIN specific loadings were rather low ( $34\text{--}154 \text{ kg N km}^{-2} \text{ yr}^{-1}$  in average),  $\text{P-PO}_4$  specific loadings were elevated ( $3\text{--}28 \text{ kg P km}^{-2} \text{ yr}^{-1}$  in average). These masses may also be considered elevated compared to Mediterranean Rivers (e.g., EEA, 1999; Ludwig et al., 2009). Even though levels of  $\text{PO}_4$  were important in Seybouse outlet waters, the specific loadings in the catchment were paradoxically low ( $2\text{--}15 \text{ kg P km}^{-2} \text{ yr}^{-1}$ ). The low loadings in DIN of Mafragh estuary compared to Seybouse one, is not only because of the smaller human population in the watershed, but may also be linked to the buffering effect of the Mafragh marshland, which provides nutrient sinks. The loadings of  $\text{Si-Si}(\text{OH})_4$  were remarkably comparable between the two estuaries in both wet and dry years. In addition to the heavy nutrient loads introduced into the Bay, especially via Seybouse, the loading ratios of  $\text{DIN}:\text{PO}_4$  ( $>30$ ) and  $\text{Si}(\text{OH})_4$ :DIN ( $<1$ ), were also unbalanced, suggesting that P and Si may be the limiting factors for coastal phytoplankton growth.

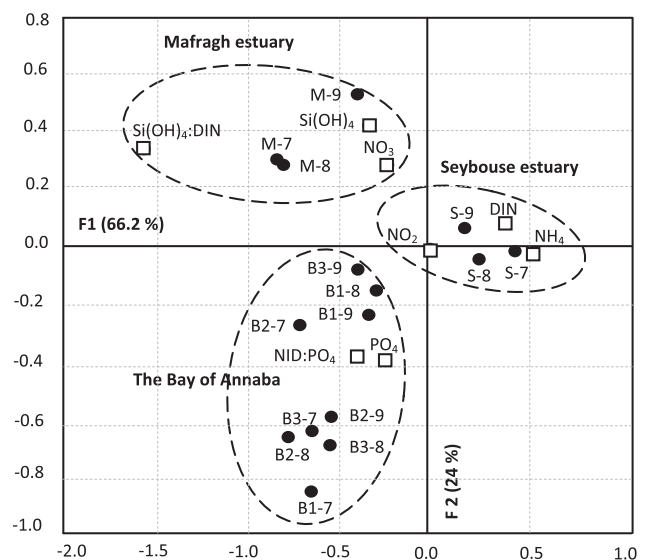
#### 4.2. The bay

The disturbed estuarine inputs have strong effects on impact the adjacent coastal water. The estuary plumes of Seybouse and Mafragh always show high levels compared to the outer waters, where nutrient levels declined 3-fold for DIN and  $\text{Si}(\text{OH})_4$  and by 2-fold for  $\text{PO}_4$ . The Seybouse plume was highly enriched by  $\text{NH}_4$  ( $2.8\text{--}7 \mu\text{M}$ ) and by  $\text{PO}_4$  ( $1\text{--}2.2 \mu\text{M}$ ) throughout the seasons, depending on estuarine inputs. These spatial distributions have also been reported by Frehi et al. (2007) and Ounissi and Frehi (1999).

Compared to the Bay of Annaba, the Bay of Algiers (e.g., Samson-Kechacha, 1981; Bachari Houma, 2009) is less enriched with all nutrients, where  $\text{NO}_3$ ,  $\text{Si}(\text{OH})_4$  and  $\text{PO}_4$  varied respectively in the range of  $0.1\text{--}5 \mu\text{M}$ ,  $0.1\text{--}5 \mu\text{M}$  and  $0.05\text{--}0.8 \mu\text{M}$ . At other similar Mediterranean coastal waters, for example the Bay of Tunis, Tunisia (Daly Yahia-Kafi et al., 2005); the Bay of Izmir, Turkey (Kucuksezgin et al., 2006), the Bay of Strymonikos, Greece (Sylaios

et al., 2006), the Catalan coastal inner waters, Spain (Flo et al., 2011), the Bay of Annaba show comparable spatial and temporal tendencies of nutrient concentrations. The inner bays directly submitted to continental discharge, are always markedly enriched. However, the outer waters showed different enrichment according to local hydrological conditions. Besides river and domestic wastes input, the Bay of Annaba receives direct industrial wastes (from a great fertilizer factory) highly loaded with  $\text{NH}_4$  ( $200 \mu\text{M}$ ,  $1.8 \text{ tons day}^{-1}$ ) and  $\text{PO}_4$  ( $30 \mu\text{M}$ ,  $0.9 \text{ ton day}^{-1}$ ), which affect the water quality of the receiving coastal water (Ounissi et al., 2008) in particular the N:P ratio. These loadings may represent about 300,000–400,000 inhabitant-equivalent.

These observations confirmed the findings of the correspondence analysis (CA). The factorial plan  $\text{F1} \times \text{F2}$  of the CA provides 90.2% of the total inertia, where the first factor (F1) contributes 66.2% and the second factor (F2) 24% (Fig. 8). The first factor is mainly explained by the variables  $\text{NH}_4$ ,  $\text{PO}_4$  and  $\text{Si}(\text{OH})_4$ :DIN, which are associated with Seybouse and Mafragh estuary observation. The Seybouse discharge was characterized by high level of  $\text{NH}_4$  and DIN, as opposed to the Mafragh waters that were richer in  $\text{Si}(\text{OH})_4$  and  $\text{NO}_3$ , and with high  $\text{Si}(\text{OH})_4$ :DIN ratios. These two continental nutrient sources also stand in contrast to the  $\text{DIN}:\text{PO}_4$  ratio, which was lower in Mafragh estuarine inputs. The second factor is explained mainly by the levels of  $\text{Si}(\text{OH})_4$  and the  $\text{Si}(\text{OH})_4$ :DIN ratio as distributed in the Mafragh estuary and in the Bay. The of Mafragh estuary contributes to explain the F2 because of its high  $\text{Si}(\text{OH})_4$  levels and  $\text{Si}(\text{OH})_4$ :DIN ratio. These features are opposed to the coastal waters, that are richer in DIN than  $\text{PO}_4$  and their  $\text{DIN}:\text{PO}_4$  ratio is more under the influence of the Seybouse estuary, which is strongly enriched by DIN and  $\text{NH}_4$  (Fig. 8). Overall, the first factor may represent the anthropogenic effects from Seybouse estuary with its heavy load of DIN and  $\text{PO}_4$  and low  $\text{Si}(\text{OH})_4$  due to damming, as has been reported in contiguous catchments (Ounissi and Bouchareb, 2013). The second factor may represent the effect of the Mafragh estuary, which seems to play a positive role by



**Fig. 8.** Factorial plan projection  $\text{F1} \times \text{F2}$  of the correspondence analysis showing the three segregated areas: F1, the Seybouse estuary with levels of high DIN forms level in contrast to the Mafragh estuary characterized by high levels in  $\text{SiO}_4$ ,  $\text{NO}_3$  and elevated  $\text{SiO}_4$ :DIN ratio; F2, the bay stations both have distinct chemical characters. The variables are  $\text{NH}_4$ ;  $\text{NO}_2$ ;  $\text{NO}_3$ ;  $\text{Si}(\text{OH})_4$ ;  $\text{Si}(\text{OH})_4$ :DIN;  $\text{DIN}:\text{PO}_4$ . The objects or sites surveyed in the years 2007; 2008 and 2009 are designated as follows: S-7; S-8; and S-9 for the Seybouse estuary outlet for the years 2007; 2008 and 2009; M-7; M-8; and M-9 for the Mafragh estuary outlet for the years 2007; 2008 and 2009; B1-7; B1-8; B1-9; B2-7; B2-8; B2-9; B3-7; B3-8; and B3-9 for the stations of the Bay. B1, B2 and B3 were surveyed in the years 2007, 2008 and 2009.

enriching the adjacent coastal waters. However, the Seybouse estuary clearly affected the quality of the major contiguous marine waters because of the eastward current (Fig. 1) that brings the water mass to the eastern part of the Bay (Ounissi and Frehi, 1999).

In addition, there was obvious inter-annual variability in nutrient levels as well as seasonal cycles at all spatial scales. These variations in coastal nutrient followed the hydrological cycle of estuarine nutrient and water discharge. The wet years of 2007 and 2009 had more elevated nutrient values and in water discharge while the salinity values decreased significantly according to the freshwater inputs. In the wet years, the Redfield ratios were also more balanced especially for DIN:PO<sub>4</sub> which decreased to 16 and 20 within the estuarine plumes of Seybouse and Mafragh, respectively. These hydrological conditions did not clearly affect the Si(OH)<sub>4</sub>:DIN ratio, which remained near the standard Redfield ratio value (1:1). This suggests that the continental inputs in the wet periods were more enriched in DIN over Si(OH)<sub>4</sub> and that Si(OH)<sub>4</sub>:DIN increased in the dry years. In the inner Bay, Frehi et al. (2007) and Ounissi and Frehi (1999) reported that the estuarine discharge delivered more DIN than Si(OH)<sub>4</sub>, which lead to the appearance of harmful species such as *Dinophysis* spp. and *Alexandrium* spp., despite the spring bloom of *Noctiluca miliaris* and other protists such as the *Tintinnids Favella* spp.

Despite the direct anthropogenic influence on river flow, large-scale processes (meteorological pattern, weather patterns, large scale indices) impact the variability of the riverine nutrient discharges and that of the nutrients in the bay. The north Atlantic oscillation (NAO), with centers of action near Iceland and the Azores, has long been identified as an influencing factor on Mediterranean climate variability, especially during winter (Ulbrich et al., 2012). The positive winter NAO is related to below-average precipitation rates over large parts of the western and northern Mediterranean region, with opposite deviations for the negative winter NAO (Trigo et al., 2004, 2006). The Mediterranean atmospheric winter water deficit is positively correlated with the NAO and has been increasing due to the long-term positive anomalies of the NAO since the early 1970s (Mariotti et al., 2002). Links of Mediterranean climate variability to tropical circulation anomalies have been identified. The most important one is the relation to the El Niño Southern Oscillation (ENSO), whose signals from the tropical Pacific area can be propagated downstream as a Rossby-wave train (Alpert et al., 2006), thus affecting regions like the Mediterranean region, far away from the Pacific origin of the dynamical signal. Correlations between ENSO and western Mediterranean rainfall have been found for spring and autumn, but with opposite signs: spring rainfall following ENSO warm events is decreased (Mariotti et al., 2002), whereas autumn rainfall preceding the mature warm phase of ENSO is increased (Mariotti et al., 2005). Over the 50-years period the Mediterranean atmospheric water deficit increased by about 24% in the winter season, and by 9% annually (Mariotti et al., 2002). In contiguous Algerian catchments (North-eastern Algeria), Meddi et al. (2010) reported a decrease of at least 20% of total annual rainfall from the mid-1970s. River discharges with their loads of nutrients into Mediterranean Sea are then doubly affected by the climatic variability and by dams retention. These factors can modulate the eutrophication impact upon these sensitive coastal systems.

## 5. Conclusions

This work may improve our picture of nutrient inputs into the Mediterranean Sea, because it provides the distribution and nutrient loads of two important Algerian estuaries and their impact on the receiving coastal water quality for the first time. The Seybouse estuary inputs were rich in PO<sub>4</sub> and NH<sub>4</sub> compared to other

Mediterranean Rivers, where NO<sub>3</sub> generally dominates. The DIN-specific loadings from the Seybouse outlet may be considered among the highest of Mediterranean Rivers. Both estuaries' outlets were impoverished in Si(OH)<sub>4</sub> because of the estuarine buffering and retention by reservoirs. The quality of the water that was introduced into the Bay of Annaba was also reflected in the unbalanced Redfield molar ratios. The Si(OH)<sub>4</sub>:DIN ratio for Seybouse waters was low in all seasons, rarely exceeding 0.5, in contrast to the Mafragh waters which had consistently balanced Si(OH)<sub>4</sub>:DIN. The lowering of Si(OH)<sub>4</sub> levels in the Mafragh estuary did not affect the Si(OH)<sub>4</sub>:DIN ratio, which remained almost balanced because DIN inputs were limited in this more pristine watershed. The Mafragh estuary may be a good example of Si(OH)<sub>4</sub>:DIN molar ratio that is mainly controlled by human nitrogen inputs rather than retention in estuaries or reservoirs. Therefore, controlling nitrogen inputs in catchments seems to be of primary importance compared to lowering by dam construction to allow more Si passage, in particular for Mediterranean sub-arid regions. The Mafragh estuary appears to be less impacted in terms of NH<sub>4</sub> and PO<sub>4</sub>; it can play a positive role by introducing clean waters that may mitigate the highly polluted Seybouse inputs. In wet years, the Redfield ratios were more balanced in the inner Bay stations. At the marine stations, because of estuarine inputs, the DIN:PO<sub>4</sub> and Si(OH)<sub>4</sub>:DIN ratios were below the Redfield standard values in 60% of samples.

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