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Intitule

Dissolved nutrient (N, P, Si) and particulate matter transfer from the Seybouse and Mafragh estuaries

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HIGHLIGHTS

We assessed both the contribution of riverine and wet atmospheric inputs of materials into Annaba Bay, Algeria.

- Wet atmospheric deposition over Annaba area is characterized by strong concentration and yields of PO_4 and SiO_4, which are several-fold the average Mediterranean values.
- Rainwater yields of dissolved nitrogen were remarkably low, compared to the average Mediterranean values.
- Particulate matter (POC, Chl a, BSi) displayed significant yields especially for Mafragh River catchment.
- Seybouse River waters still highly charged with NH4 and PO4 with unbalanced N:P and Si:N ratios in almost of samples.

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ABSTRACT

ABSTRACT

This study simultaneously assesses for the first time the relative contributions of both riverine and wet atmospheric inputs of materials into the Algerian Annaba Bay on the North Africa Mediterranean coast. Surface water sampling and water discharge estimates were performed weekly in 2014 at the outlets of the Mafragh River (MR) and Seybouse River (SR) into the bay. Rainwater samples were collected jointly on a daily basis at a close meteorological station, where precipitation data were monitored. Riverine and rainwater samples were analyzed for dissolved nutrients (nitrogen: N, phosphorus: P and silicon: Si). The particulate matter in the riverine samples was also analyzed for suspended particulate matter (SPM), particulate organic carbon (POC), biogenic silica (BSi), chlorophyll *a* (Chl *a*), particulate organic nitrogen (PON) and particulate organic phosphorus (POP). The rainwater from the Annaba region was characterized by high concentrations of phosphate (PO_4) and silicate (SiO_4) that are several times the average Mediterranean values and yield strong deposition fluxes. Conversely, the levels of dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON) and associated fluxes were remarkably low. The dissolved nutrient fluxes for the two catchments were low following the lowering of the river flows, but those of particulate matter (POC, Chl *a*, BSi) displayed significant amounts, especially for the MR catchment. BSi and POP represented approximately a third of the total silicon and total phosphorus fluxes, respectively. MR water had levels of dissolved N and P comparable to those of rainwater and appeared to be a nearly pristine ecosystem with low nutrient levels and almost balanced N:P and Si:N ratios. SR water had low SiO_4 levels but was highly charged with NH_4 and PO_4 and showed unbalanced N:P and Si:N ratios in almost all samples. These conditions have resulted in large phytoplankton biomasses, which may lead to eutrophication problems. More importantly, the rainwater was determined to be a relevant source of fertilizers for marine waters and agricultural land in the Annaba area and can partially balance the loss of SiO_4 from rivers to the bay due to dam retention.

Key words:

Atmospheric deposition, River input, Annaba Bay, Nutrients, Mediterranean Sea

RESUME

Cette étude évalue simultanément pour la première fois les flux des rivières et des dépôts atmosphériques humide des matériaux dans la baie d'Annaba algérienne sur la côte méditerranéenne de l'Afrique du Nord. Des échantillonnages d'eau de surface et des estimations de débit d'eau ont été réalisés chaque semaine en 2014 aux embouchures des rivière de Mafragh (MR) et de Seybouse (SR). Les échantillons d'eau de pluie ont été collectés conjointement tous les jours dans une station météorologique dans laquelle les données de précipitation ont été surveillées. Les échantillons de rivière et d'eau de pluie ont été analysés pour les nutriments dissous (azote: N, phosphore: P et silicium: Si). La matière particulaire dans les échantillons d'eau de rivière ont également été analysée pour la matière en suspension (SPM), le carbone organique particulaire (COP), le silicium biogènique (BSi), la chlorophylle *a* (Chl a), l'azote organique particulaire (NOP) et le phosphore organique particulaire (POP). L'eau de pluie de la région d'Annaba est caractérisées par des concentrations élevées de phosphate (PO_4) et de silicate (SiO_4) ces valeurs sont plusieurs fois supérieur à la moyenne méditerranéenne et produisent des flux importants. À l'inverse, les concentrations d'azote inorganique dissous (NID) et d'azote organique dissous (NOD) et les flux associés étaient remarquablement faibles. Les flux de nutriments dissous pour les deux bassins versants étaient faibles suite à la réduction des débits des rivières, mais les flux des matières particules (COP, Chl *a*, BSi) ont présentées des quantités importantes, en particulier pour le bassin de MR. BSi et POP représentaient environ un tiers des flux totaux de silicium et de phosphore total, respectivement. L'eau de MR avait des niveaux de N et P dissous comparables à ceux de l'eau de pluie et semblaient être un écosystème presque vierge avec de faibles niveaux de nutriments et des rapports N: P et Si: N presque équilibrés. L'eau de SR avait des niveaux faibles de SiO_4 mais était très chargée en NH_4 et PO_4, des rapports N: P et Si: N déséquilibrés dans presque tous les échantillons. Ces conditions ont entraîné une grande biomasse de phytoplanctonique, ce qui peut causer des problèmes d'eutrophisation. L'eau de pluie a été déterminée comme une source importante d'engrais pour les eaux marines et les terres agricoles dans la région d'Annaba et peut compenser partiellement la perte de SiO_4 retenu dans les rivières des barrages.

Les mots clés :

Nutriments, déposition atmosphérique, flux des rivières, Baie d'Annaba, la Méditerranée

ملخص

تقوم هذه الدراسة في وقت واحد بتقييم المساهمات النسبية لكل من المدخلات النهرية والرطبة في الغلاف الجوي للمواد في خليج عنابة الجزائري على ساحل شمال أفريقيا المتوسطي. أجريت تقديرات لأخذ العينات من المياه السطحية وتقدير المياه أسبوعياً في 2014 في منافذ نهر Mafragh (MR) ونهر Seybouse (SR) في الخليج. تم جمع عينات مياه الأمطار بصورة مشتركة في محطة أرصاد جوية قريبة، حيث تم رصد بيانات هطول الأمطار. تم تحليل عينات مياه نهر ومياه الأمطار للمواد الغذائية الذائبة (النيتروجين: N، الفوسفور: P والسيليكون: Si). كما تم تحليل الجسيمات في العينات النهرية من أجل الجسيمات العالقة (SPM)، والكربون العضوي الجزيئي (POC)، والسليكا الحيوية (BSi)، والكلوروفيل a (Chl *a*)، والنيتروجين العضوي الجسيمي (PON) والفسفور العضوي الجسيمي (POP). تميزت مياه الأمطار من منطقة عنابة بتركيزات عالية من الفوسفات (PO_4) والسلكيات (SiO_4) التي تعد عدة مرات متوسط قيم البحر المتوسط وتنتج تدفقات قوية للترسيب. وعلى العكس من ذلك، كانت مستويات النيتروجين غير العضوي المذاب (DIN) والنيتروجين العضوي المذاب (DON) والتدفق المصاحب منخفضة للغاية. كانت تدفقات المغذيات المذابة في المستجمعين منخفضة بعد انخفاض تدفقات الأنهار، ولكن تدفقات المواد الجسيمية (POC، Chl *a*، BSi) أظهرت كميات كبيرة، خاصة بالنسبة لمجمع MR. تمثل BSi وPOP ما يقرب من ثلث إجمالي تدفق السيليكون والفسفور الكلي، على التوالي. كان لدى مياه MR مستويات من N و P المذابة مماثلة لمستويات مياه الأمطار، ويبدو أنها نظام بيئي نظيف تمامًا يحتوي على مستويات منخفضة من المغذيات ونسب متوازنة تقريبًا N:P و Si:N. كانت المياه SR تحتوي على مستويات SiO_4 منخفضة ولكنها كانت مشحونة بدرجة عالية مع NH_4 و PO_4 وأظهرت نسب N و P و Si:N غير متوازنة في جميع العينات تقريبًا. وقد أسفرت هذه الظروف عن وجود كتل حيوية كبيرة من العوالق النباتية، مما قد يؤدي إلى مشاكل في المغذيات. والأهم من ذلك، أن مياه الأمطار كانت مصممة لتكون مصدرًا مناسبًا للأسمدة للمياه البحرية والأراضي الزراعية في منطقة عنابة، ويمكن أن توازن جزئياً فقدان السليسيوم من الأنهار إلى الخليج بسبب احتجاز السد.

الكلمات المفتاحية

الترسب الجوي، مدخل النهر، خليج عنابة، المغذيات، البحر الأبيض المتوسط

INTRODUCTION

INTRODUCTION

The Mediterranean Sea is one of the most oligotrophic seas in the world, where external inputs of nutrients are especially important to sustaining primary productivity (Margalef, 1985; Béthoux et al., 1998). Mediterranean coastal waters are submitted to various material inputs, from riverine, atmospheric and Atlantic water sources (Martin et al., 1989; Béthoux et al., 1998; Ludwig et al., 2010; Durrieu de Madron et al., 2011). Riverine water discharge has declined in the last 50 years (Milliman, 2006; Ludwig et al., 2009) because of increases in reservoir building (Lehner et al., 2011), demographic growth (CIHEAM, 2009), intensification of agricultural practices, and decreasing trends in precipitation (UNEP/MAP, 2013). The decreases in river discharge are leading to the oligotrophication of some Mediterranean areas (Umani et al., 2004) and may affect the primary production of those areas. Extensive River damming in the Mediterranean region has far-reaching impacts on coastal food webs (Boero et al., 2008). In contrast, coastal eutrophication is a consequence of unbalanced riverine nutrient inputs, with excess nitrogen and phosphorus with respect to silica, when compared with the requirements of diatom growth (Conley et al., 1993; Billen and Garnier, 2007).

Nevertheless, both rivers and coastal areas are facing severe anthropogenic pressures due to intense demographic, economic and ecological pressures. They are particularly sensitive to various human-induced alterations that include nutrient enrichment, organic carbon loading, chemical contamination, fisheries overexploitation, freshwater diversions, and habitat loss and alteration (Turley et al., 1999; Newton et al., 2012). In particular, nutrient loads have been significantly increased by human activity, particularly waste discharges and agricultural intensification in rivers throughout the world (Seitzinger et al., 2005; Statham, 2012). For Mediterranean rivers, Ludwig et al. (2009) reported that dissolved inorganic nitrogen (N) and phosphorus (P) inputs to the Mediterranean Sea may have increased several-fold, and in contrast dissolved silica (Si) levels is expected to decrease due to extensive dam building (Lehner et al., 2011), which enhances siliceous sediments retention rates (Humborg et al., 2000; Dürr et al., 2011). Such human perturbations affect riverine discharges of dissolved silica, leading to decrease Si:N and Si:P in receiving coastal waters and subsequent limitations in diatom growth and marine and estuarine phytoplankton composition and productivity (Humborg et al., 2000; Ragueneau et al., 2006). The molar ratios of N:P:Si have often been used to assess coastal and marine health, and 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 (Howarth and Marino, 2006; Bilen and Garnier, 2007; Glibert et al., 2012). Aquatic ecosystems can undergo fundamental food web changes as diatom growth is disturbed when the Si:N ratio falls below 1:1 (Turner et al., 1998). However, studies of river and estuarine modifications at global or regional scales remain lacking (Meybeck, 2003; UNEP/MAP, 2013) and assessing impacts of some river or estuarine syndromes on aquatic resources is considered a first priority.

Most of the nutrients entering the Mediterranean Sea derive from atmospheric wet and dry depositions and riverine runoff (Martin et al., 1989; Krom et al., 2010; Koçak, 2015). But because riverine nutrients are removed by biological activity in estuarine and adjacent coastal waters, atmospheric inputs are probably the main source of nitrogen to the open sea, even in northern zones of the Mediterranean (Guerzoni and Molinaroli, 2005; Koçak et al., 2010; Pasqueron de Frommervault et al., 2015). In the Southwestern Mediterranean Sea, atmospheric inputs of nutrients are becoming the most effective external source due to declining river discharge in recent decades from reservoir construction and changes in irrigation practices (Guerzoni et al., 1999; Guerzoni and Molinaroli, 2005). It has been reported that atmospheric inputs of nitrogen equal the riverine inputs for the entire Mediterranean Sea (Martin et al., 1989; Loÿe-Pilot et al., 1990) and are dominant in the southern zones (Bashkin et al., 1997). Im et al. (2013) observed that atmospheric deposition provides significant amounts of nutrients to continental and marine ecosystems, and in oligotrophic marine ecosystems such as the Mediterranean Sea, atmospheric deposition of nitrogen may account for up to 35-60% of new production (Christodoulaki et al., 2013). In addition, Pacciaroni and Crispi (2007) estimated that the atmospheric deposition of nitrogen and phosphorus accounted for approximately 9% and 38% of the total primary production in the Western and Eastern Mediterranean, respectively. According to Koçak et al. (2010), the atmospheric deposition of inorganic nitrogen and phosphorus largely dominated the riverine inputs for eastern Mediterranean oligotrophic waters. A number of studies along Mediterranean coasts indicate that atmospheric deposition is expected to strongly influence nutrient cycles and the biogeochemistry and trophic status of the Mediterranean Sea (Ridame and Guieu, 2002; Herut et al., 2005; Markaki et al., 2010; Violaki et al., 2010; Christodoulaki et al., 2013; koçak, 2015). For the Mediterranean, wet atmospheric deposition (through rain washout) of N and P is the main source (Guerzoni

et al., 1992; Markaki et al., 2003) in comparison with dry deposition (direct sinking or sedimentation during periods without rain). The majority of wet depositions occurred during a few intense events, which were episodic and spatially patchy (Guerzoni et al., 1999). In addition, the Mediterranean Sea, particularly its southwestern side, is subject to the largest and most persistent aerosol sources, which primarily originate from North Africa (Morales-Baquero et al., 2013; Varga et al., 2014; Vincent et al., 2015).

Moreover, nutrient inputs from both atmospheric and riverine sources into Mediterranean waters are still rare and have not been simultaneously assessed yet for southwestern Mediterranean regions. To our knowledge, the only available data on simultaneous dissolved inorganic nutrient measurements of riverine and atmospheric inputs are found in the overview of Martin et al. (1989) on the Western Mediterranean and the work of Koçak et al. (2010) on the North Levantine Sea (Turkey). Despite the importance of those reference works, the dissolved and particulate forms of N, P and Si have not been considered together for riverine water, as well as dissolved organic nitrogen (DON) for rainwater. Nevertheless, according to Markaki et al. (2003), both DON and DOP are important contributors of N and P deposition and represent almost 30% of the total dissolved atmospheric nitrogen and phosphorus load in rainwater. The contribution of DON in stimulating new production in the Eastern Mediterranean was estimated to reach 20-30% (Violaki et al., 2010), and DON represented 23% of the total dissolved nitrogen. In addition, few studies have monitored Si deposition (e.g., Markaki et al., 2010) despite its important role as a plant nutrient and carbon dioxide regulator (Sommer et al., 2006). In addition, as both organic (dissolved and particulate) and inorganic forms of nitrogen are rapidly available for sustaining marine phytoplankton (Wiegner and Seitzinger, 2001), they should consequently be considered together when assessing imbalances of riverine nutrient inputs (Billen and Garnier, 2007). Similarly, within phosphorus compounds, particulate inorganic phosphorus represents a significant fraction, a large part of which is desorb and remobilize in estuarine and marine environments (Conley et al., 1995). Moreover, a significant flux of biogenic particulate silica (derived either from endogenous diatoms or phytoliths eroded from catchment top soils) is also delivered by rivers (Garnier et al., 2002; Sferratore et al., 2006), but that form is seldom measured in monitoring programs. More importantly, silica data are missing from most monitoring programs for Mediterranean rivers (UNEP/MAP, 2013), particularly for Algerian coastal rivers (Ounissi and Bouchareb,

2013; Ounissi et al., 2014). It is clear that both organic and inorganic forms of nutrients should be considered in either riverine or atmospheric inputs to obtain a more representative picture of Mediterranean marine ecosystem productivity and biogeochemical cycles.

Information on riverine and atmospheric inputs of materials is still scarce in the Mediterranean basin (Ludwig et al., 2010; Markaki et al., 2010; Violaki et al., 2010; UNEP/MAP, 2013), but is particularly lacking for Algerian coastal catchments (Ounissi et al., 2014). From the atmosphere side, the Annaba coastal region (northwestern Algeria, is subject to atmospheric deposition under the main influences of European airflows (October-March) and African air masses with high dust loads (April-September). From the landside, it receives inputs from two important rivers in Algeria, the Mafragh River (MR) and the Seybouse River (SR). This region is consider among the wettest areas in Algeria (Laborde et al., 2010). Although the wet atmospheric deposition (WAD) of dissolved nutrients has been recognized as significant in the Mediterranean Sea, data on nutrient wet deposition on Algerian coasts are almost nonexistent. In addition, little is known about nutrient and material transport from Algerian coastal catchments (Ounissi and Bouchareb, 2013; Ounissi et al., 2014). The major efforts have focused on the groundwater quality of the SR and MR catchments, but the surface waters in those areas have only been explored for dissolved nutrients (Ounissi and Bouchareb, 2013; Ounissi et al., 2014; Ounissi et al., 2016). Due to the specific objectives of those previous studies, particulate matter was not considered, although it is a key component in river and estuarine systems.

The present work based on an extensive riverine and rainwater data collection during 2014 in the Annaba coastal area of the southwestern Mediterranean. We present the distribution and fluxes of dissolved and particulate material into the Annaba Bay from the Mafragh and Seybouse Rivers simultaneously with the wet atmospheric deposition (WAD) of dissolved nutrients. To our knowledge, this is the first work to assess the wet atmospheric deposition of dissolved nutrients on one side, and, on the other side, consider particulate matter (particulate biogenic silica, particulate organic carbon, suspended particulate matter and chlorophyll *a*) in southwestern Mediterranean waters, including Algerian coastal waters.

The main objectives of this study were to:

1. Assess the relative contributions of riverine and wet atmospheric inputs of dissolved nutrients (N, P, and Si) into Annaba Bay.
2. Determine the relative importance of the dissolved and particulate matter transferred into the bay through the two rivers' outlets.
3. Assess differences in the material deliveries of the two rivers' outlets, which are differently, affect by human activities.

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The manuscript is structured in three chapters: the first one is strictly documentary which provides an overview on (i) the Mediterranean sea, (ii) the Northern Algeria air masses and precipitation, (iii) Atmospheric deposition of nutrients, (iv) the riverine water discharge quality and the biogeochemistry of nutrients (N, P, Si) and particulate organic matter composition and characteristics. The second chapter describes the study sites and sampling methods and chemical analyses in both riverine and atmospheric deposition. The third chapter presents the results of riverine inputs of dissolved nutrients (N, P, Si) and particulate organic matter (POC, BSi, Chl *a*) into Annaba Bay and the differences in material deliveries between Mafragh and Seybouse estuaries differently affected by human activities. The forth chapter provides the results of atmospheric deposition of dissolved nutrients (N, P, Si) level and flux. The fifth chapter compares the riverine and wet atmospheric inputs in the Mediterranean and several coastal ecosystems. Each analytic chapter ends by a relevant discussion, weighting and focusing our own results regarding the appropriate literature findings. Finally, the manuscript lasts with conclusion that gives the main finding of this work.

CHAPTER I
COASTAL ENVIRNEMENT FEATURES

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COSTAL ENVIRONMENT FEATURES

1. Characteristics of the Mediterranean Sea (MS)

The Mediterranean Sea is the largest semi-enclosed sea on the Earth covering about 2.5 10^6 km^2 with an average water depth of about 1.5 km. It is located between Europe, northern of Africa and West Asia and stretches from the Strait of Gibraltar on the west to the Dardanelles and the Suez Canal on the east. The MS is usually divided into two different basins: the Western Basin and the Eastern Basin. The Western Basin extends from the Cape of Trafalgar in Spain and the Cape of Spartel in Africa in the west to Tunisia's Cape Bon in the east. The Eastern Basin stretches from the eastern boundary of the Western Basin to the coasts of Syria and Palestine.

The Mediterranean region was an important route for merchants and travelers of ancient times, allowing for trade and cultural exchange, and today it is a notable contributor to global economy and trade. Its coasts support a high density of inhabitants, distributed in 21 states, and it is one of the top tourist destinations in the world, with 200 million tourists per year (Coll et al., 2010). The Mediterranean Sea connects through the Strait of Gibraltar to the Atlantic Ocean in the west and through the Dardanelles to the Sea of Marmara and the Black Sea in the northeast. In the southeast, the Suez Canal links the Mediterranean to the Red Sea and the Indian Ocean.

The climate in the region is characterized by hot dry summers and cool humid winters. The annual mean sea surface temperature shows a high seasonality and important gradients from west to east and north to south (Hopkins, 1985). An estimation of the water mass balance shows that the Mediterranean Sea has a negative hydrological balance with loss through evaporation exceeding the input of water through runoff and precipitation. This deficiency is mainly compensated by the flow of Atlantic Water through the Strait of Gibraltar and the Dardanelles (Stamou and Kamizoulis, 2009). Evaporation is higher in its eastern half, causing the water level to decrease and salinity to increase from west to east.

Besides the main thermohaline circulation, several local features characterize the Mediterranean circulation, such as gyres and fronts. Atlantic Water is present almost everywhere in the basin (Fig. 1). It forms two anticyclonic gyres in the Alboran Sea, constrained by the bathymetry, and then bifurcates around the Sardinia Island in two different branches: one into the Tyrrhenian Sea as the source of the large scale cyclonic

circulation occurring in the north western Mediterranean (Fig. 1). The other crosses the Sicilian Channel and penetrates in the Ionian Sea. The water from the Tyrrhenian produces a large cyclonic circulation in the western Mediterranean, with the central gyre between the Balearic Islands and the Sardinia being the region of deep water convection (Fig. 1).

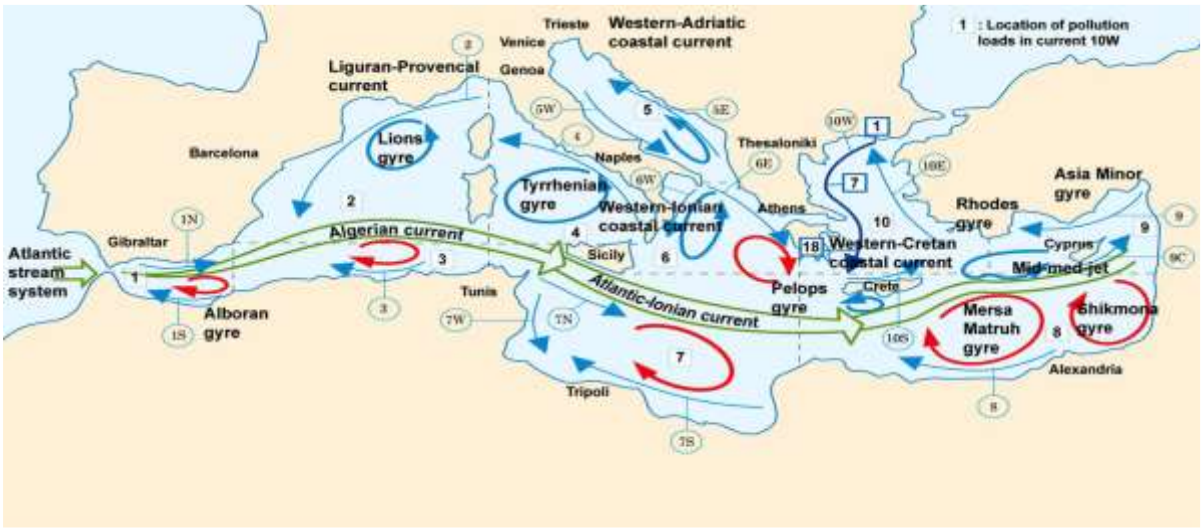

Figure 1. The 10 areas of the Mediterranean Sea and the 18 coastal currents (from Stamou and Kamizoulis, 2009).

The MS is one of the most oligotrophic surface wasters in the world with Low Nutrient and Low Chlorophyll concentrations (Koçak et al., 2010). The principal reason for this oligotrophication is that the Mediterranean has an anti-estuarine circulation in which nutrient poor surface waters incoming from the Atlantic is balanced by outgoing relatively nutrient rich deep waters of the MS through the Strait of Gibraltar (Hamad et al., 2005). Most of the nutrients entering the MS originate from atmospheric depositions and riverine inputs (Krom et al., 2010; Koçak et al., 2015). Because a significant reduction (20%) in rivers freshwater discharge, atmospheric inputs are probably the main source of nitrogen to the open sea, even in northern zones of the Mediterranean (Guerzoni and Molinaroli, 2005; Koçak et al., 2010; Pasqueron de Frommervault et al., 2015). The basin is characterized by strong environmental gradients (Danovaro et al., 1999), in which the eastern end is more oligotrophic than the western. The biological production decreases from north to south and west to east and is inversely related to the increase in temperature and salinity.

The recent marine biota in the MS is primarily derived from the Atlantic Ocean, but the wide range of the climate and hydrology have contributed to the co-occurrence and

survival of both temperate and subtropical organisms (Sara, 1985; Bianchi and Morri, 2000). High percentages of Mediterranean marine species are endemic (Boudouresque, 2004; Tortonese, 1985). This sea has as well its own set of emblematic species of conservation concern, such as sea turtles, several cetaceans, and the critically endangered Mediterranean monk seal (*Monachus monachus*). It is the main spawning grounds of the eastern Atlantic blue fin tuna (*Thunnus thynnus*) (Delaugerre, 1987; Mackenzie et al., 2009). There are several unique and endangered habitats, including the seagrass meadows of the endemic *Posidonia oceanica*, vermetid reefs built by the endemic gastropod *Dendropoma petraeum*, coralligenous assemblages (Green and Short, 2003) and deep-sea and pelagic habitats that support unique species and ecosystems (Sarda`et al., 2004). Many sensitive habitats exist within the coastal ecosystems. There are 150 wetlands of international importance for marine and migrating birds, and some 5000 islands and islets (Blondel and Aronson, 2005).

2. Climate and precipitation over the North of Algeria

Northern Algeria covers about 227 740 km^2, situated in the southwestern region of the Mediterranean Basin. Bound by Morocco to the west, Tunisia to the east, and the Saharan Desert to the south. The northern part of Algeria, is characterized by a Mediterranean climate with relatively cold and rainy winters, and hot and dry summers. Climate in northern Algeria is influenced by the Mediterranean Sea in the north and Saharan in the south. The relief increase from west to east in the North of Algeria, producing unequal rainfall patterns between the regions from west to east and from south to north (Fig. 2) (Laborde, 1993; Meddi, 1992; Meddi et al., 2016; Taibi et al., 2015). Annual rainfall reaches 400 mm in the west, 800 mm in the center and 1000 mm in the eastern coastal region (Fig. 2).

The two main factors controlling the variability of rainfall in the Mediterranean basin are the North Atlantic Oscillation (NAO) in most of the Western Mediterranean region (Xoplaki et al., 2000; Trigo et al., 2004), and the El Niño-Southern Oscillation (ENSO) in the Eastern Mediterranean, where the influence of NAO is weak (Yakir et al.,1996).

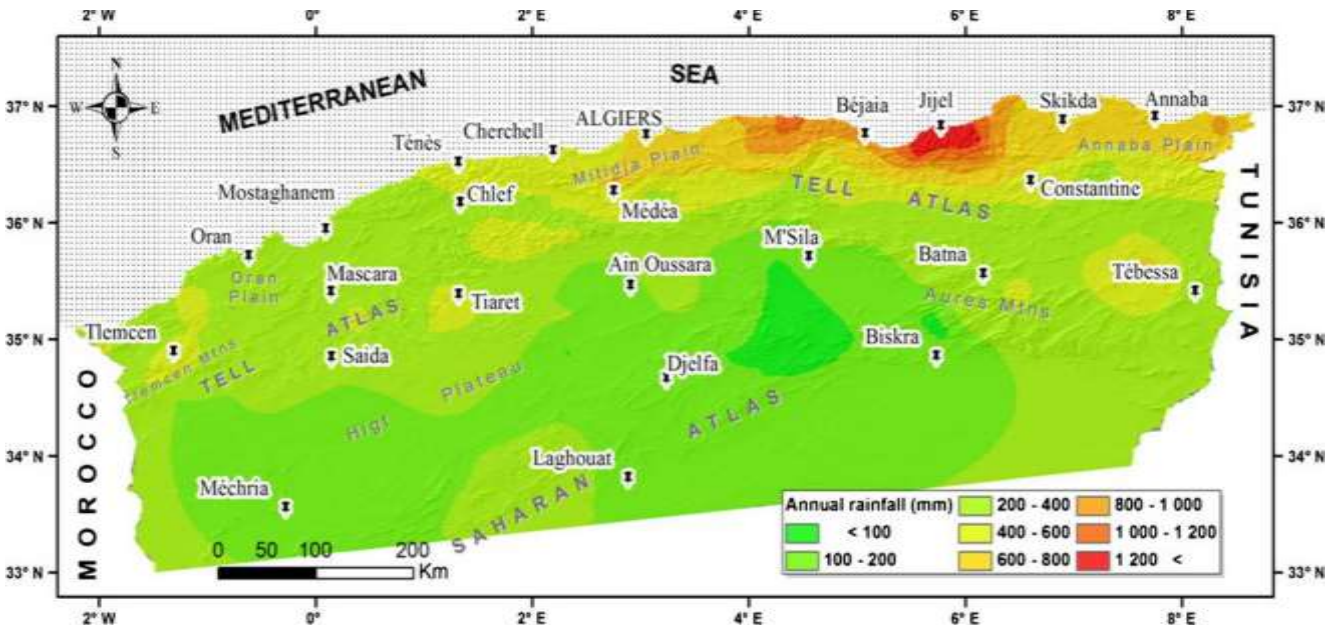

Figure 2. Map of annual rainfall in Northern Algeria in (mm), from Meddi et al. (2016).

The north Atlantic oscillation (NAO), with centers of action near Iceland and the Azores (Fig. 3), is identifying as an influencing factor on the Mediterranean climate variability, principally during winter (Ulbrich et al., 2012). The NAO has two phases, positive phase (Fig. 3) when the contrast between high pressure over the Azores and low pressure in the far north Atlantic is stronger than normal, the NAO is said to be in a positive phase. This usually drives mild Atlantic storms into northern Europe but keeps the Mediterranean region comparatively dry.

However, when the contrast is lower than normal, the NAO becomes negative and opens the door to cold, dry Arctic intrusions into northern Europe and wet, slow-moving systems across the south (Fig. 3).

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 (Fig. 4), 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 (Fig. 4).

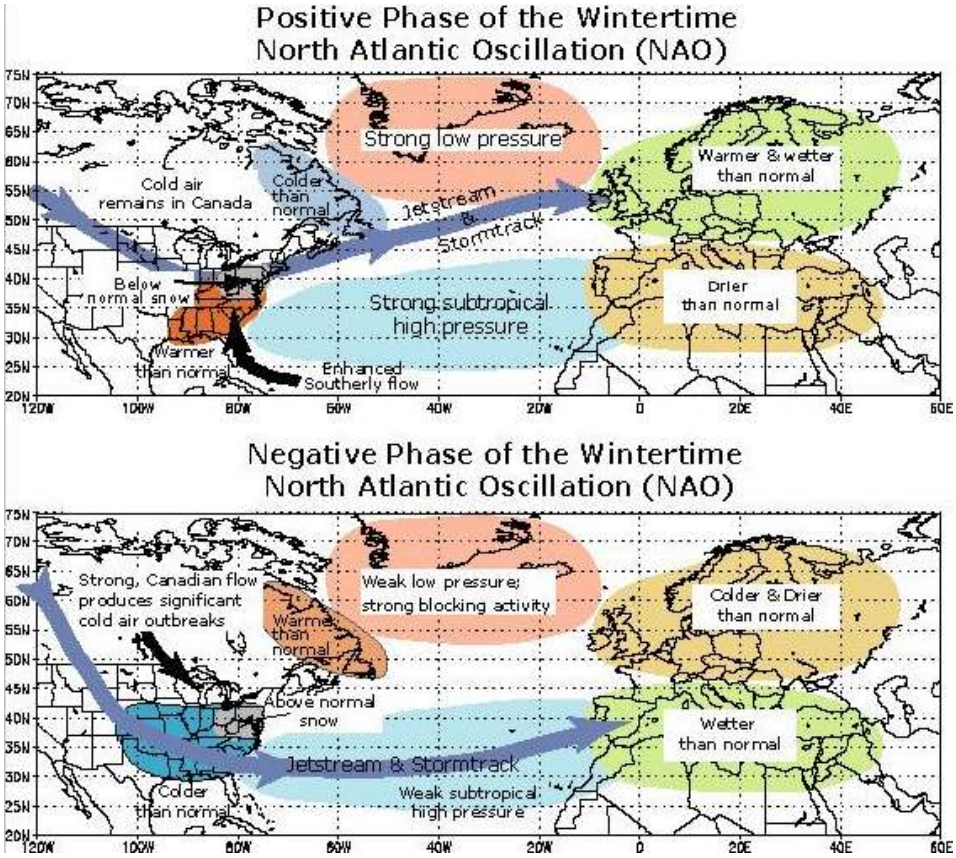

Figure 3. Conditions typically associated with the North Atlantic Oscillation (NAO) during wintertime. From: https://www.weather.gov/iwx/la_nina.

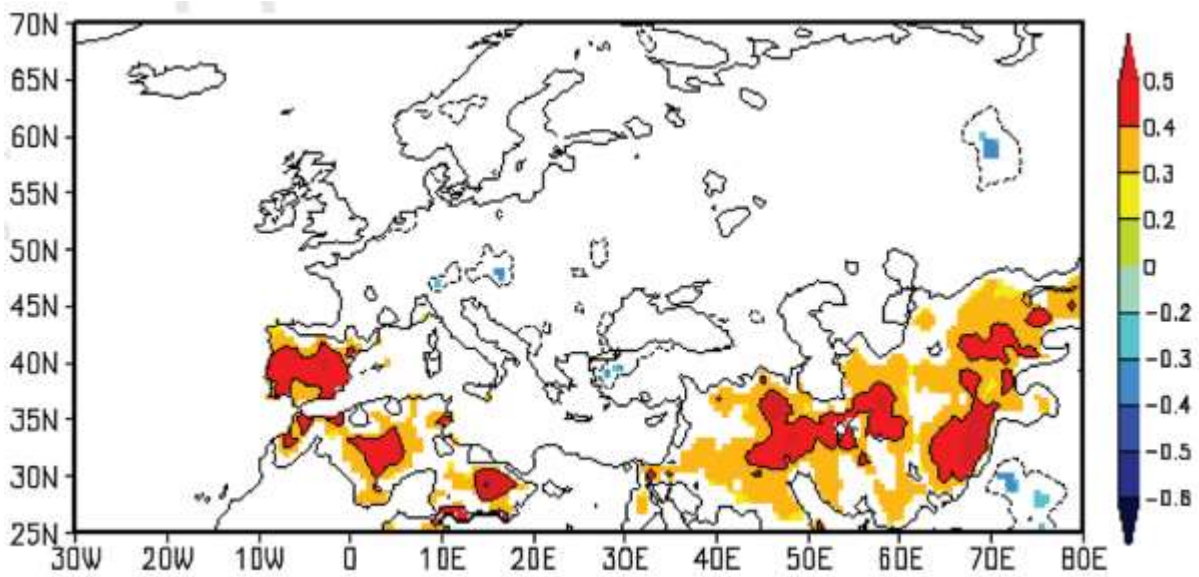

Figure 4. Correlations between Euro-Asian autumn rainfall and El Niño indices for the period 1948–2000 (from Alpert et al., 2006).

3. Biogeochemical importance and impacts of atmospheric deposition on marine systems

Wet atmospheric deposition input is a major source for the transport of natural and anthropogenic elements from continents to the sea (Duce et al., 1991; Jickells, 1995). The two main sources affect the composition of atmospheric precipitation in the Mediterranean region are, eolian dust transported from North Africa (Guerzoni et al., 1999; Kubilay and Saydam, 1995) and the other one is the pollution aerosol transported from Europe (Dulac et al., 1987; Bergametti et al., 1989; Gullu et al., 1998).

Mediterranean basin receives important amount of anthropogenic aerosols from industrial and domestic activities in populated region mostly from Europe (Migon and Sandroni, 1999). According to Guerzoni et al., (1999), wet atmospheric deposition participate with 66% of the total nitrogen enriching Mediterranean Sea. Unlike the nitrogen compounds, which have dominant anthropogenic sources (Spokes and Jickells, 2005) Mediterranean Sea receives a noticeable flux of dust derived from Sahara Desert (Guerzoni et al., 1999). This Saharan dust was charged with phosphorus (PO_4) and silicon (Si) component are natural continental origin like rocks, soil and sand (Herut et al., 1999; Markaki et al., 2003) (Fig. 5).

During spring and summertime from April to September (Varga et al., 2014), the atmosphere of the Mediterranean Basin is highly charged with dust emission originated from the African Sahara (Fig. 5). Due to the activity of dust source areas as emitters of windblown mineral particles, about several hundred thousand tons of Saharan dust transported northward effect the Mediterranean biogeochemistry (Herut et al., 1999; Ridame and Guieu, 2002; Markaki et al., 2003; Varga et al., 2014).

Through the stratification phase, atmospheric inputs can be the main external nutrient supply to offshore surface waters (Bartoli et al., 2005; Guieu et al., 2010), and episodes of Saharan dust deposition can develop primary production (Ridame and Guieu, 2002), and influence the composition of phytoplankton community (Bonnet et al., 2006). In the eastern Mediterranean Sea, atmospheric inputs account for 60–100% of the bioavailable nitrogen and for 30–50% of the bioavailable phosphorus (Krom et al., 2004).

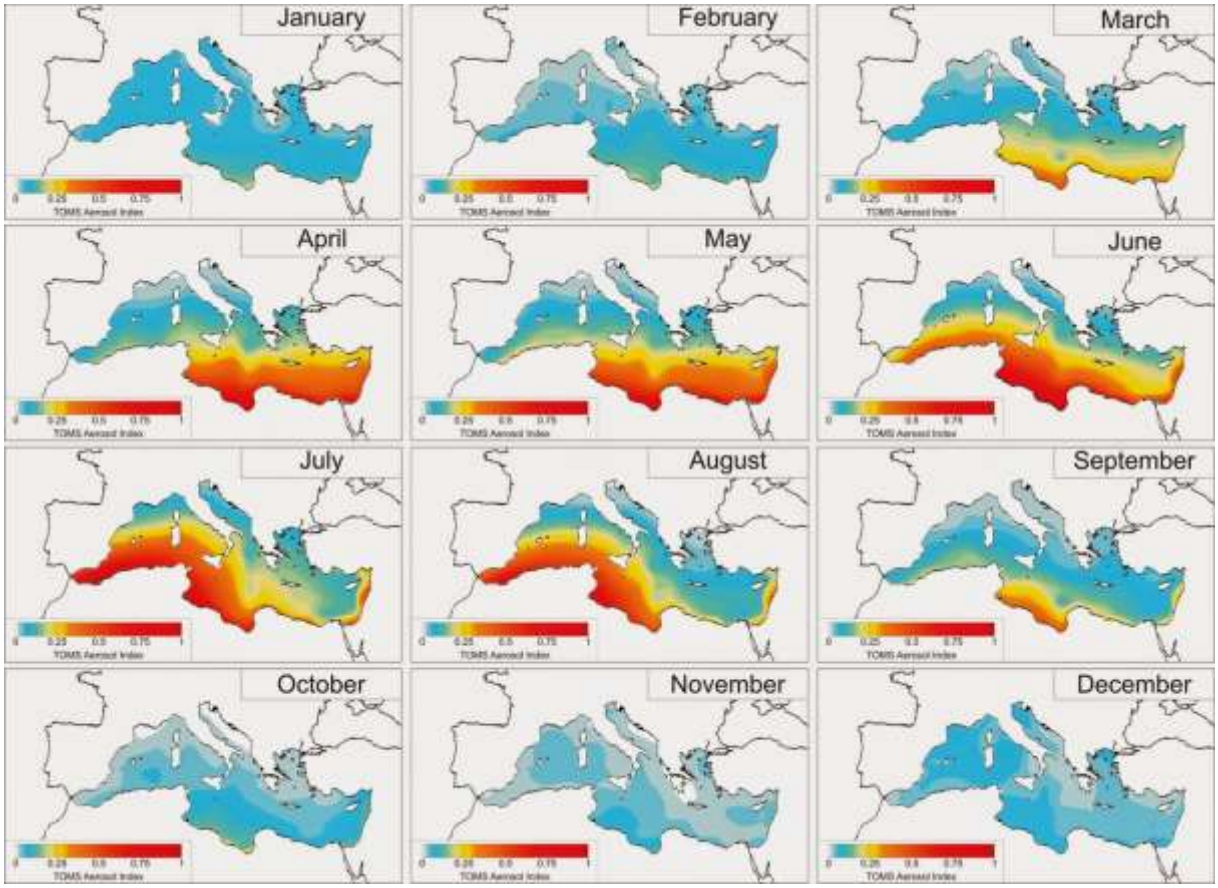

Figure 5. Saharan dust in the Mediterranean region (From Varga et al., 2014).

4. Rivers and estuaries (discharge)

Estuaries are semi-enclosed bodies of water, situated at the interface between land and ocean (Fig. 6), where seawater is measurably diluted by the inflow of freshwater (Hobbie, 2000). The term "estuary," derived from the Latin word aestuarium, means marsh or channel (Webster, 1979). Because of their unique location at the interface between terrestrial freshwater and the sea (Fig. 6), estuaries are dynamic transition zones (Toublanc et al., 2016; Mclusky, 1971; Bazin et al., 2014) acting as important geochemical and biological filters and transformers of nutrients passing from catchments to the sea (Church, 1986; Teuchies et al., 2013).

The estuaries which are located in microtidal regions are of relatively recent origin, having commenced their formation during the Holocene marine transgression only about 7000 years ago (Cooper, 2001; Roy et al., 2001). Under low river flow and low rainfall events, estuaries are separated from the sea for several months through the formation of sand bars across their mouths (Hodgkin and Lenanton, 1981; Potter and Hyndes, 1999).

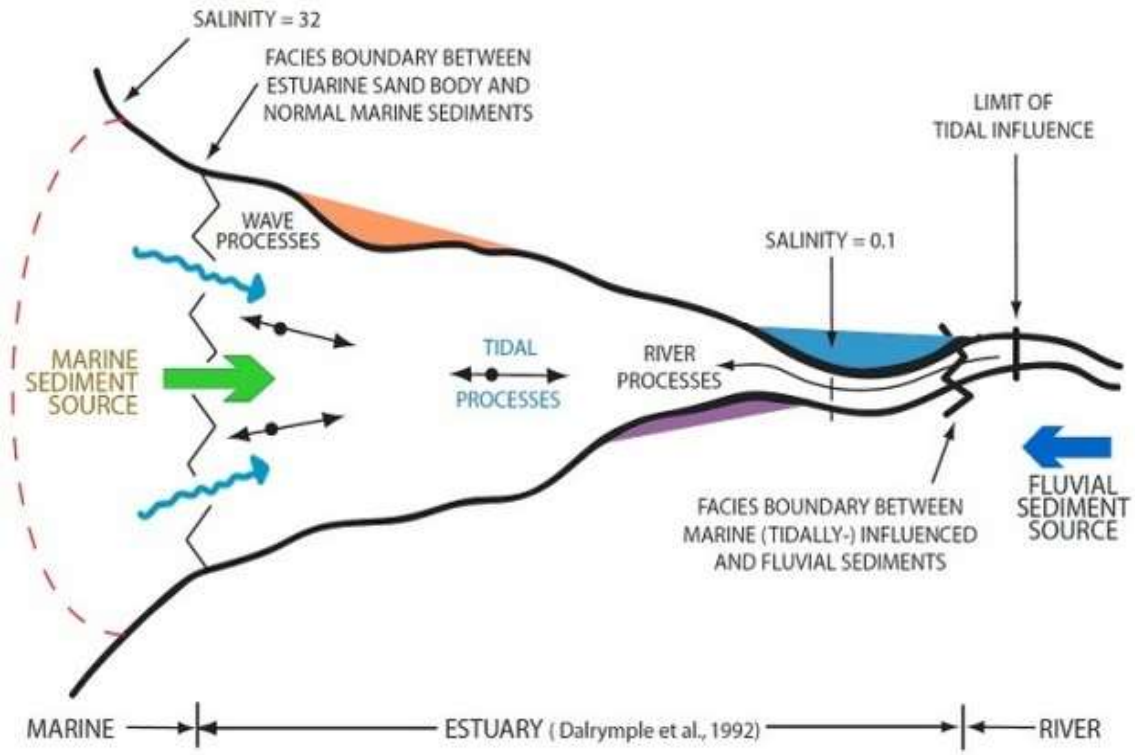

Figure 6. Classic estuarine zonation Modified (from Bianchi et al., 2006).

The sand bars are naturally or artificially breached in winter or spring seasons under the increase of volume water in the estuary because of the heavy rainfall that occurs in the region during those seasons (Ranasinghe and Pattiaratchi, 1999). Estuaries are among the most productive and precious ecosystems in the Earth. Estuaries have high economic and ecological values: migration routes and reproduction zones, nutrient regulation, trapper and filter and recycle suspended particulate matter, detoxification of polluted waters, breeding areas for terrestrial populations, preferential sites for commercial fishes, tourism and recreation, transportation, supply of food and energy resources. This precious ecosystem facing severe anthropogenic pressures, being under intense demographic, economic and ecological pressures. Including eutrophication, chemical contamination, fisheries overexploitation, introduced species (Kennish, 2002).

5. The Mediterranean Rivers Bassin

Rivers are important sources of freshwater and nutrients for the Mediterranean Sea (Fig. 7). Rivers annually inject around 300 km^3 of continental water in to Mediterranean sea, where about 50% of this volume delivered by the 10 biggest Mediterranean rivers

(Ludwig et al., 2009; Durrieu de Madron et al., 2011; UNEP/MAP 2015). The Rhône and Pô Rivers provided the largest freshwater discharge, accounting for about 25% of the total continental freshwater discharge (Fig. 7).

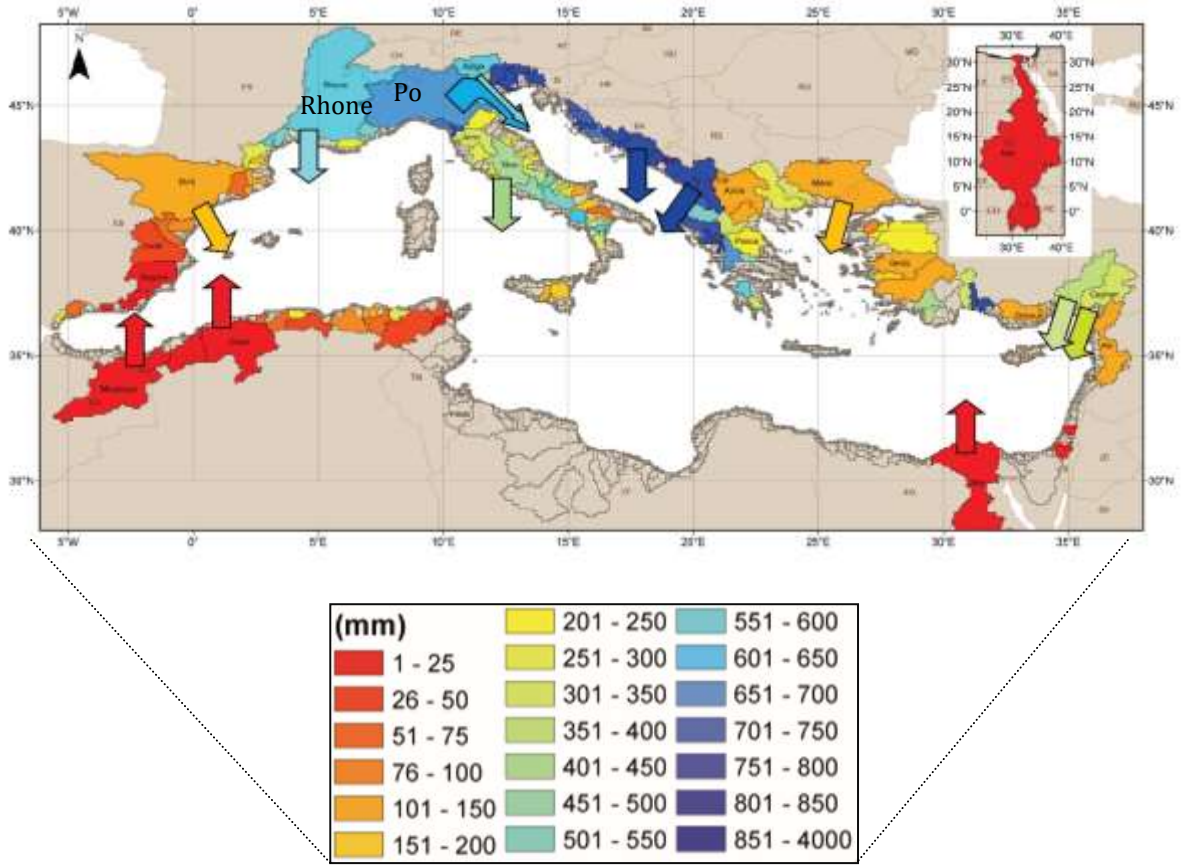

Figure 7. Annual river discharger into the Mediterranean Sea (from UNEP/MAP, 2015).

Mediterranean rivers suffer from a significant reduction (20%) in freshwater discharge in the 50 years (Milliman, 2006; Ludwig et al., 2009) due to reservoirs retention (Lehner et al., 2011; Ounissi et al., 2013), demographic growth (CIHEAM, 2009), increase of agricultural practices, and decreasing trends in precipitation (UNEP/MAP, 2013). A reduction of the river freshwater discharge implies a reduction of the fluxes of dissolved silica (Si) originating from natural sources such as erosion. In contrast, the fluxes of nitrogen (N) and phosphorus (P) were significantly increased by human activity, particularly waste discharges and agricultural intensification, in rivers (Fig. 8) throughout the world (Seitzinger et al., 2005; Statham, 2012), leading to increased pressure on estuarine and coastal ecosystems (Jickells, 1998; Diaz and Rosenberg, 2008).

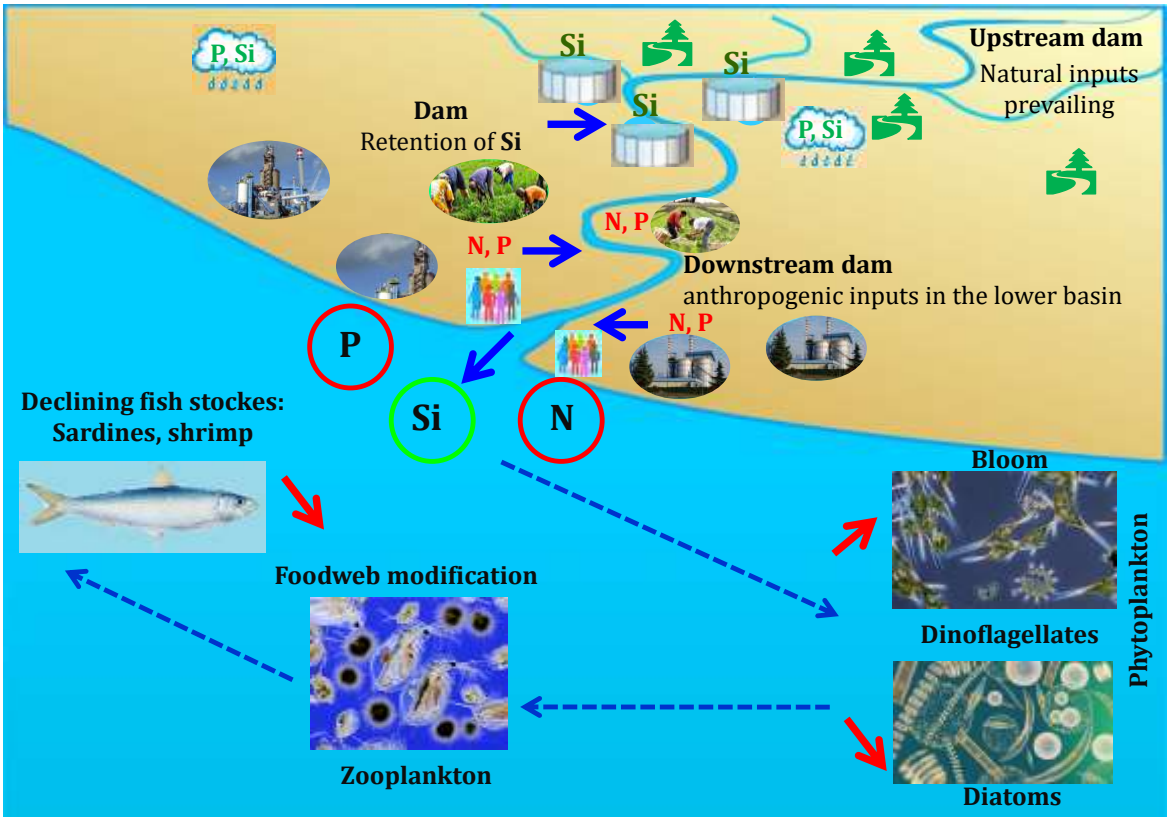

Figure 8. Diagram simplified the impacts of human activities on the chemistry of continental waters and on the coastal functioning and productivity.

These biogeochemical modifications are responsible for many negative impacts: loss of habitat and biodiversity, increased proliferation of harmful phytoplankton species, eutrophication, and hypoxia (Ragueneau et al., 2006; Billen et Garnier, 2007; Howarth et al., 1996). In the same context, Turner et al. (2003) reported that the decrease in the Si:N ratio causes severe changes in the coastal food web including fisheries (Fig. 8). In the Mediterranean, it is admitted that Si can not only reduce productivity, but also induce changes in phytoplankton communities with dominance of non-siliceous harmful species (Fig. 8). Similarly, Turner et al. (1998), Turner et al. (2003) and Cloern (2001) demonstrate that the decrease in the abundance of diatoms and copepods in coastal areas is linked to the reduction of Si Rivers inputs (Fig. 8). These changes in the composition of phytoplankton affect the entire coastal system including the decline of coastal fishery resources.

6. Materials in rivers

6.1. Total solids (TS)

Total Solids (TS), are the total of all solids in a water sample. They include the suspended solids (TSS) or suspend particulate matter (SPM), dissolved solids (TDS). The total dissolved solids (TDS), are the fraction of total material that passes through a membrane filter with a nominal pore size of (0.45 µm). In contrast, the total suspended solids (TSS) or suspend particulate matter (SPM) retained by the filter of (0.45 µm). Dissolved solids (TDS) consist of sodium (Na^+), calcium (ca^{2+}), potassium (K^+), chlorides (cl^-), nitrate (NO_3^-), phosphorus (PO_4^{3-}), sulfur (SO_4^{2-}), and other ions. Suspended solids include silt and clay particles, plankton, algae, fine organic debris, and other particulate matter: biogenic silica (BSi), particulate organic phosphorus (POP), particulate organic nitrogen (PON), particulate organic carbon (POC) and chlorophyll (chl*a*).

Total solids have been identified as major source of pollutant of lakes, rivers and estuaries in both dissolved and particulate forms. Total solids in coastal water result from erosion from urban runoff and agricultural land, industrial wastes, bank erosion, bottom feeders (such as carp), algae growth or wastewater discharges and atmospheric transport (Taamalah et al., 2016).

Total suspended solids (TSS), regulate transparency of water, depth of the photic zone, and regulate primary and secondary production. They also regulate the production of bacterioplankton and the mineralization and consumption of the oxygen content (Håkanson, 2006). Soil erosion constitute a serious danger for Mediterranean soils (UNEP/PB, 2003), when the action of water was intensive, the solid charge becomes important (5-130 g L^{-1}) and erosion becomes significant (Roose, 1991). Water erosion causes soil degradation, which is closely related to nutrient losses either in, the soluble form or adsorbed to soil particles (Bertol et al., 2007). The loss of nutrients by water erosion in catchments contributes to soil degradation (Bertol, 1994; Schick et al., 2000). Nutrients (N, P, K Ca, and Mg) are the main nutrients that restore soil fertility and are subject to losses by water erosion (Schick et al., 2000). In contrary, the superabundant concentrations of nutrients in water resulting from water erosion are leading to salinisation, acidification, eutrophication or pollution by toxic substances.

6.2. Silicon

The major source of dissolved silicon to river water and estuaries is from weathering of terrigenous rock minerals by naturally acidic rainwater (Drever, 1997). In estuarine and marine systems the dissolved form of silicon is silicic acid ($Si(OH)_4$). Silicon (Si) is an essential elemental requirement for some phytoplankton species diatoms, radiolarians, silicoflagellates, and siliceous sponges, which utilize dissolved silica (DSi) to form their structural elements of amorphous hydrated silica(Fig. 9), known as BSi or opal (Ragueneau et al., 2000; Van Cappellen et al., 2002).

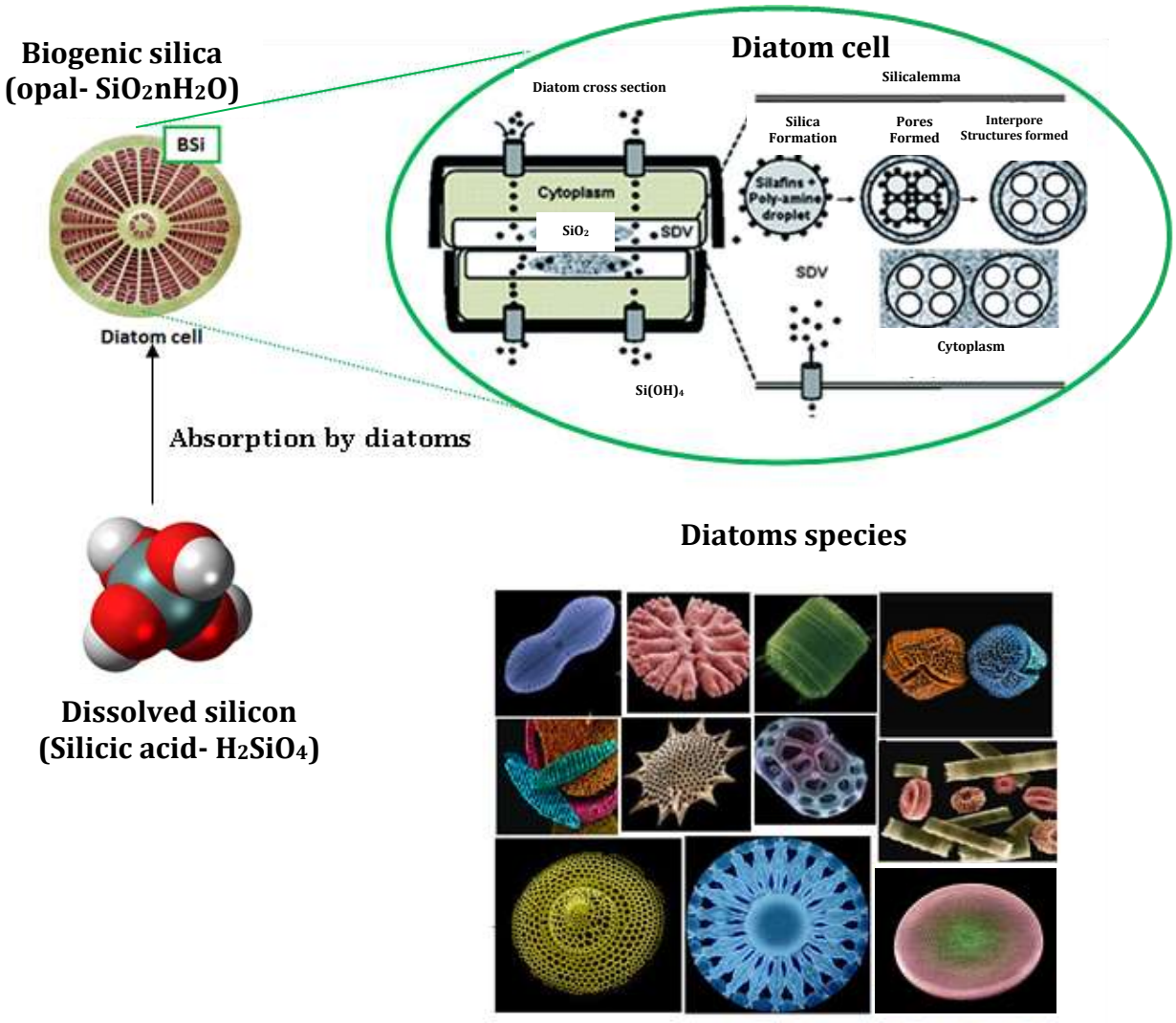

Figure 9. Absorption of silicon by diatoms.

The silicon plays a crucial role in the functioning of coastal ecosystems, especially since N and P delivery have increased (Nixon et al., 1996; Howarth et al., 1996), and Si flux has

decreased because of dam building (Conley et al., 1993) and river manipulation (Humborg et al., 1997). These factors sometimes combine, leading to decreasing Si:N and Si:P ratios in the receiving coastal waters and Si limitation of diatom growth (Ragueneau et al., 2002).

Silicates play a crucial role in the global cycling of matter particularly in the carbon cycle. It contributes doubly to the elimination of atmospheric carbon:

(1) Leaching according to the reaction where carbon is transferred and stored in marine biogeosystems:

$$CaAl_2Si_2O_8 + 2CO_2 + 8H_2O \rightarrow Ca^{2+} + 2Al(OH)_3 + 2H_4SiO_4 + 2HCO_3^-$$

(2) Elimination in the seabed as diatom mud Rousseau et al. (2002) demonstrated experimentally that the diatoms are differently silicified where the Si:C ratio varies between 0.2 and 0.74. In fact, the role of the sea in the Global Carbon storage is directly coupled to the global silicon cycle, because diatoms (microscopic vegetal plankton) using Si in their shells, actually form 60% of the global phytoplankton (Tréguer et al., 1995; Ragueneau et al., 2000; Yool and Tyrrell, 2003). Diatoms absorb atmospheric CO2 dissolved in sea water and nutrients (N, P and Si) to produce their own organic material and their envelope formed essentially of Si according to the reaction:

$$106CO_2 + 121H_2O + 15NH_3 + 15\ SiH_4O_4 + H_3PO_4 \rightarrow 106(CH_2O)15(NH_3)15Si(OH)_4H_3PO4$$

The elimination of organic carbon by diatoms is at the rate of 1 mol of Si to 7moles of C. Consequently, any increase in Si inputs to the sea is accompanied by an increase in the carbon flux in marine sediments and therefore implies the elimination of large amounts of atmospheric carbon (as shown in reaction 2). The flux variations of Si Rivers to the sea are dependent on lithology, erosion rate, climate and production of diatoms (Conley, 1997). Finally, it could be said in fact that “What Carbon is to biosphere, Silica is to lithosphere” (Sommer et al., 2006).

6.3. Phosphorus

Phosphorus is a vital element (Karl, 2000), it plays important roles in living cells as a constituent of genetic materials (DNA, RNA) as well as building of cell walls (phospholipids) compounds and energy transfer (ATP). In Rivers, more than 90 % is associated with particulate matter (Meybeck, 1982).

Phosphorus is exists in both dissolved (<0.45 µm) and particulate (>0.45 µm) forms, each of which contain organic and inorganic forms (Yoshimura et al., 2007; Cai and Guo, 2009). Total dissolved P (TDP) usually is defined as that fraction passing through 0.1–1 µm poresized filters, is partitioned into dissolved inorganic P (DIP), and dissolved organic P (DOP). The DIP pool consists of orthophosphate (PO_4), pyrophosphate and polyphosphate (P_2O_5). Inorganic dissolved DIP is dominated by orthophosphoric (H_3PO_4) acid that is protonated to varying degrees depending on the ionic composition of the water. Total particulate P (TP) also exists in inorganic P (PIP) and organic P (POP) forms. Anthropogenic sources of P include sewage, agricultural discharges, and detergents in wastewaters.

6.4. Nitrogen

In aquatic environment system, Nitrogen exists in both dissolved (<0.45 µm) and particulate (>0.45 µm) forms. Dissolved inorganic nitrogen (DIN) formed by ammonium (NH_4), nitrate (NO_3) and nitrite (NO_2). Dissolved organic nitrogen (DON) is composed essentially of urea, free dissolved amino acids, complex dissolved amino acids, proteins, nucleic acids and their derivatives, enzymes and humic acids (Le Gal, 1989). Total particulate N (TN) also exists in inorganic nitrogen (PIN) and organic nitrogen (PON) forms. Ammonium (NH_4) in surface waters comes mainly from agricultural, domestic waste, and industrial discharges. In the low oxygen environment, NH_4 dominates due to the reduction of nitrates. Conditions of reductions and hypoxia are a sign of pollution. Nitrates often come from the nitrification of organic nitrogen, land drained by surface water, chemical fertilizers from agricultural waste, of urban, industries and farming areas. In the aquatic environment, DON derived from the metabolism of microorganisms, cell lysis, and decomposition of organic matter. It is used by bacteria as a nitrogen source and regenerated in mineral form (DIN) absorbed by plants. The available forms for primary producers such as phytoplankton are NO_3, NH_4, but also the DON. However, ammonium is the preferred form to the phytoplankton because it is energetically less expensive and directly converted into amino acids using the glutamate dehydrogenase enzyme (Bougis, 1974).

6.5. Particulate organic carbon

Particulate organic matter (POM) in estuarine systems divided into autochthonous and allochthonous inputs (Darnell, 1967). Organic matter exists in both dissolved and particulate forms (Fig. 10). Usually measured as dissolved organic carbon (DOC) and particulate organic carbon (POC). Particulate organic carbon represent about 45-50% of organic matter. This Organic material derived from terrestrial and aquatic primary producers (Meyers- Schulte and Hedges, 1986; Kirchman et al., 1991).

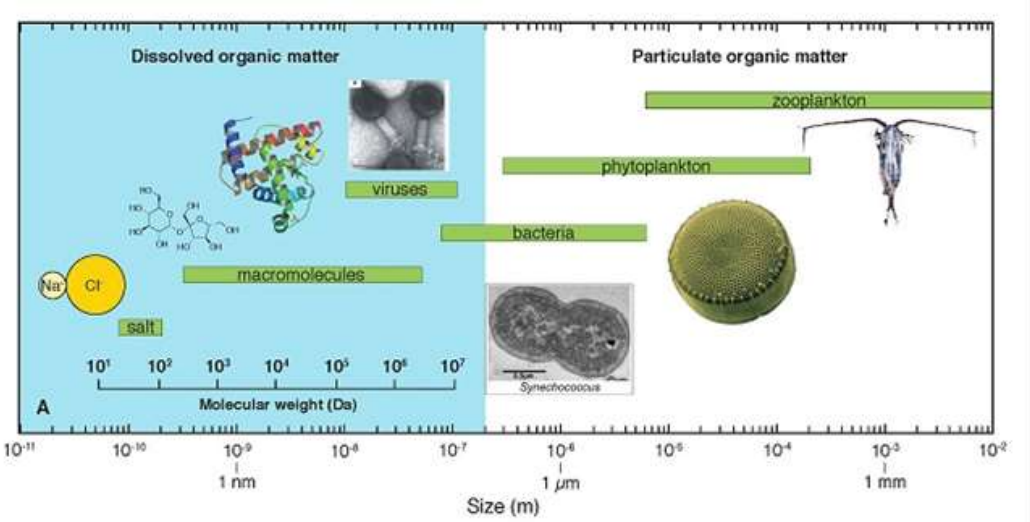

Figure 10. Size range of particulate (POM) and dissolved organic matter (DOM) and organic compounds in natural waters. https://scienceblog.com/489712/ocean-carbon-recycling-size-matters/.

Particulate organic carbon (POC) is composed of living organisms such as bacteria, phytoplankton, and zooplankton, as well as a detrital component derived from living organisms such as macrophyte detritus, zooplankton casts (Millero and Sohn, 1992).

The oceanic biological pump is a fundamental process regulating atmospheric carbon dioxide CO_2 (Martin, 1990; Volk and Hoffert, 1985).Carbon dioxide (CO_2) dissolves in seawater and becomes part of the ocean's carbonate system, whose simplified representation is:

$$CO_2+H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$$

The phytoplankton is responsible for most of the transfer of carbon dioxide from the atmosphere to the ocean. Through photosynthesis processes, phytoplankton absorb carbon dioxide (CO_2) (Fig. 11) and convert it into dissolved inorganic carbon (DIC) (Holtz et al., 2015a). This inorganic dissolved carbon (DIC) is converted in gross primary production by phytoplankton into particulate organic carbon (POC) (Fig. 11). Important amount of particulate organic carbon (POC) is autotrophically respired and converted

back into DIC. The rest stays in the form of net primary production (Holtz et al., 2015a). Some of the organic carbon sinks into the lower ocean levels as detritus or calcium carbonate in shells. Some soft tissue is converted into particulate organic carbon or dissolved organic carbon and, from these forms, into dissolved inorganic carbon. The rest sinks to the ocean floor (Holtz et al., 2015b). Shells out of calcium carbonate are also deposited on the ocean floor as sediment, whereas the carbon can dissolve and reach the lower ocean levels again (Honjo et al., 2008).

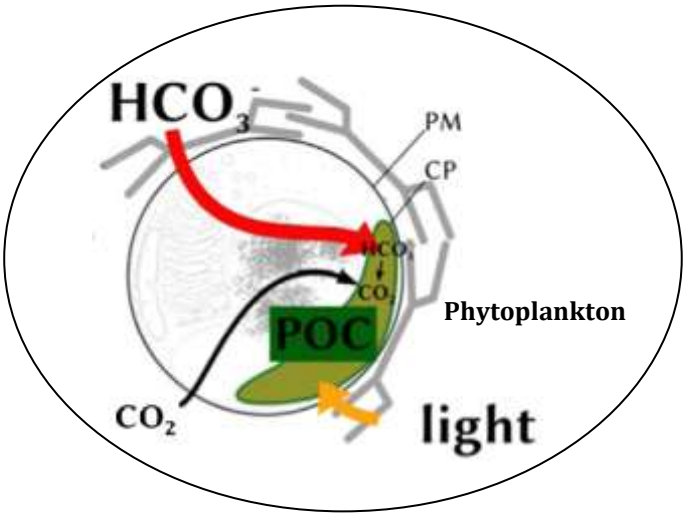

Figure 11. Production of particulate organic carbon POC by the phytoplankton cells (from Holtz et al., 2015a).

CHAPTER II

MATERIALS AND METHODS

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1. Sampling sites

Annaba Bay is located in the Northeastern part of Algeria (Fig. 12), between cape Rosa and cape garde with a surface area of 400 km^2 and a maximum depth of 70 m. The bay receives continental inputs from the Mafragh River (MR) and Seybouse River (SR) (Fig. 12) and from direct industrial and household wastes (Ounissi et al., 2008) of over 2 million people. The lower parts of SR and MR are affected by tidal intrusion during the dry season and function as highly stratified estuaries (Khélifi-Touhami et al., 2006; Ounissi et al., 2014). The salt wedge reaches up to 8 and 15 km in SR and MR, respectively (Khélifi-Touhami et al., 2006; Ounissi et al., 2014).

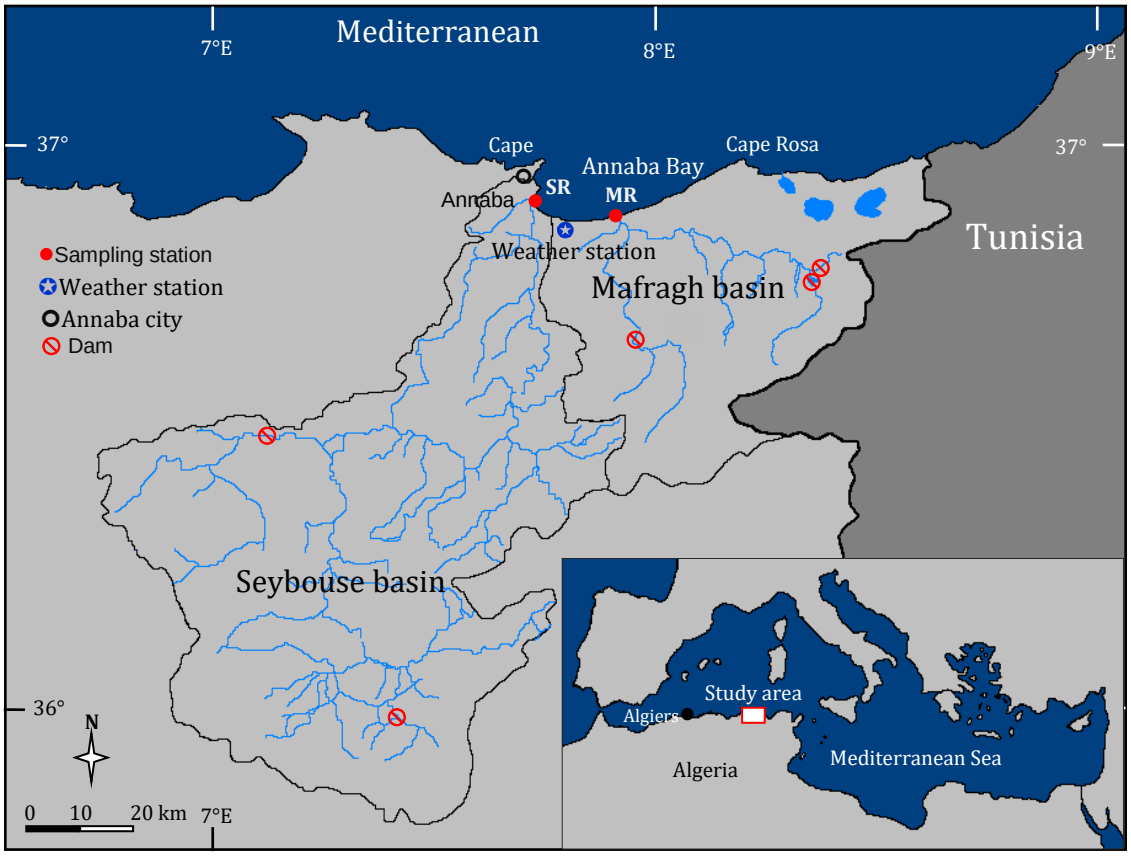

Figure 12. Map of the Seybouse River (SR) and Mafragh River (MR) catchments and their adjacent coast (Annaba Bay) showing the sampling sites (river' outlets and weather station).

With a length of 165 km and a catchment area of 6500 km^2, SR is among the largest and developed river systems in Algeria (Fig. 13), with a population of about 1.5 million inhabitants. Intensive agriculture is extending (3-4% of the total catchment area; UNEP/MAP, 2013) over the middle and the lower SR catchment, thanks to water

retention in reservoirs (400 million m^3). This amount is equivalent to third or half the annual precipitation yield

Figure 13. View of Seybouse outlet during the 2014.

The MR catchment (3200 km^2) is weakly populated (90 inhab. km^{-2}), but intensive agricultural practices is being invading most of the middle and lower catchment. Agriculture has been recently described as the most important source of nitrogen and phosphorus emissions in this area, mainly originating from irrigated area (4-5% of the total catchment; UNEP/MAP, 2013) and cow rearing, in addition to the significant road traffic (mainly to and from Tunisia).

Figure 14. View of Mafragh outlet during the 2014.

The catchment is largely forested in the upper part, but includes large marshland and floodplain (130 km^2) in the lower part (Fig. 14). During the dry season and under low river flow, the MR connection to the sea may be closed for several months (Fig. 14). Sampling sites are situated at the outlets of MR and SR, distant by about 15 km.

2. Analytical methods

2.1. Riverine water

Surface water sampling was taken every week during the year 2014, and water discharge and salinity were simultaneously measured. To assess the rivers water discharge (m^3 s^{-1}), flow velocity at the river' outlets was determined with a current meter CM-2 (Toho Dentan Co., Ltd., Tokyo), and calculated by multiplying the water velocity by the total surface area (m^2) of the river wet section. Measurements of water velocity were taken at several points of the river section; this allows computing the average current velocity. The water salinity (Practical Salinity Scale: PSS) was measured in situ with a multi-parameter probe WTW Cond 1970i. Surface water samples were collected from the middle of the river flow for nutrient and particulate organic matter analyses, and were immediatelypre-filtered after sampling using a sieve filter (200-µm porosity), except samples designated for suspended particulate matter or SPM.

In the laboratory, water samples collected for dissolved nutrient analyses were filtered through Whatman GF/C glass filters (0.5-µm porosity). The dissolved nutrients were analysed on the same or the following day. For silicates (SiO_4 or orthosilicic acid ($Si(OH)_4$) and particulate biogenic silica (BSi) determination, a fraction of each sample was filtered through polycarbonate filters. Particulate matter was stored at -20°C for one day and analyzed. The dissolved inorganic nitrogen DIN (ammonium: NH_4; nitrate: NO_3; nitrite: NO_2), dissolved organic nitrogen (DON), phosphate (PO_4)and SiO_4 were determined by means of standard colorimetric methods described in Parsons et al. (1989). The total dissolved phosphorus (TDP) and polyphosphate (P_2O_5) were measured following the standard method of Rodier (1996). Dissolved organic phosphorus (DOP) was obtained by subtracting the dissolved inorganic phosphorus (DIP = PO_4 + P_2O_5) from TDP.

Suspended particulate matter (SPM) was measured using two water subsamples of 250-500 ml (depending on the water sample turbidity), following the method described in Parsons et al. (1989).

Chlorophyll *a* (Chl *a*) level was measured according to the method of Lorenzen (1967). As the river' outlets are usually highly productive, a water sample of only 250-500 ml is filtered through a Whatman 47-mm GF/C glass filter and chlorophyll is extracted in a refrigerator for 1 hour in pure methanol.

Particulate organic carbon (POC) was determined following the titrimetric method of Le Corre (Aminot et Chaussepied, 1983). The filtered volume and filters are the same as those used for SPM. Biogenic particulate silica (BSi) was determined according to the method of Ragueneau and Tréguer (1994). The particulate biogenic silica retained on polycarbonate filters was digested to extract the corresponding SiO_4. SiO_4 level was analyzed by the standard colorimetric method described in Parsons et al. (1989).

The particulate organic nitrogen and phosphorus were measured according to Raimbault et al. (1999) method, which consisted in oxidizing organic N and P (by the action of persulfate reagent at 120°C under alkaline buffered conditions) to obtain the equivalent mineral forms (NO_3 and PO_4 respectively). NO_3 and PO_4 was determined following Parsons et al. (1989) manual.

All dissolved nutrients and particulate matter forms were analyzed on duplicate samples (or subsamples). The total phosphorus (TP) is the sum of dissolved and particulate phosphorus forms, total nitrogen (TN) is the sum of dissolved and particulate nitrogen forms, and total silica (TSi) is the sum of dissolved silica (SiO_4) and particulate biogenic silica (BSi).The relative precisions are: PO_4: ±3.4%; NH_4: ±3.3%; NO_3: ±2.6%; NO_2: ±3.7%; SiO_4: ±1.2%; DON: ±5.5%; P_2O_5: ±5.2%; TDP: ±2.7%; POC: ±5.5%; POP: ±5%; PON: ±5%; Chl *a*: ±5.2%; BSi: ±2.4%.

The annual fluxes for dissolved nutrients and particulate matter were estimated using the method of average instantaneous loads (Preston et al., 1989):

$$F = K \sum_{i=1}^{n} \left(\frac{CiQi}{n} \right)$$

where F is the annual flux (in tons per year or t yr^{-1}), Ci is the concentration of the substance of interest (µmol l^{-1} for dissolved nutrients converted to kg m^{-3} or mg l^{-1} for particulate matter), Qi is the concomitant instantaneous flow (m^3 s^{-1} converted to m^3 day^{-1}), n is the number of days with level and flow data and K is the conversion factor to consider the period (365 days) and unit of estimation. This assumes that the average

flux derived from measurements can be extrapolated to the whole year. To facilitate comparison between the two catchments, fluxes (t yr^{-1}) have been normalized by the catchment area and expressed in t km^{-2} yr^{-1}.

2.2. Rainwater

Rainwater samples were collected using a rainfall collector (200-cm^2 collecting area; 2-L collecting polyethylene bottle) placed in a cleared and fenced area of Annaba weather station (36°49′19″N, 7°48′11″E), located 3 km far from Annaba Bay coastline in between the two river mouths (Fig. 15), at 5 m above the mean sea level. The sampling site is situated in a rural area, but it is not much isolated from the main pollution sources in the region: 10 km far from Annaba city and its surrounding villages (nearly 1 million inhabitants), 5 km from the great fertilizers factory (Fertial Company) and 10 km from the Arcelor Mittal steel complex of El Hadjar. These potential pollution sources may contaminate the local atmosphere.

Figure 15. Photos of the used rain gauge. A: view of the rain gauge type Degreane Horizon with sensor equipment; B: a view of the rain gauge and other meteorological sensors of Annaba weather automatic station; C: view of the rain gauge collecting area.

A total of 100 rainfall days were recorded during 2014 at the Annaba weather station, among which 32 could be analysed. When the collected rainfall was not insufficient for all chemical analyses, the collection was diluted with distillated water to obtain the required volume.The samples were transferred into polyethylene bottles, transported to

the laboratory and analyzed in the same or the following day. Rainwater samples were treated and analyzed for different analytical determinations (NH_4, NO_3, NO_2, DON, PO_4, SiO_4) as for river water.

The wet atmospheric deposition fluxes (*Fw*) were computed following Herut et al. (1999). The volume weighted average concentration (*Cw*) in rainwater of the nutrient of interest is first computed from:

$$Cw = \frac{\sum_{i=1}^{n} Ci \, X Qi}{\sum_{i=1}^{n} Qi}$$

Where *Ci* is the nutrient concentration and *Qi* is the rainfall amount for the given precipitation event. The wet atmospheric deposition fluxes (*Fw*) of nutrients are then computed by multiplying the volume weighted average concentration of the nutrient of interest by the annual rainfall amount (P_{annual}), assuming that the average flux derived from the analysed set of samples is representative of the whole year:

$$Fw = Cw \, X \, P_{annual}$$

The 32 analysed samples represent a total of 229,7 mm (38.6%) over the annual total of 595,5 mm. They include 7 daily samples in January, 7 in March, 1 in April, 2 in May, 1 in June, 1 in July, 2 in September, 3 in October, and 8 in December, in agreement with the seasonal cycle of precipitation.

2.3. Statistical analyses

One-way analysis of variance (ANOVA) was carried out to compare the difference between weekly sampling of material in MR and SR outlets with a significance threshold at P = 0.001. Where significant differences in the one way ANOVA were detected between weekly samples a Tukey's Honestly Significantly Different (HSD) test was also applied to those samples in order to identify sources of variation. Data were statistically analyzed using SPSS statistics software version 17.0. The relationships between the various biogeochemical parameters were also studied through the correlation coefficient *r* computed using the same software. Unless specified, the number of correlated pairs is n =54. Significance threshold values at p =0.001, 0.01 and 0.05 are $|r|$ >0.42, $|r|$ >0.32 and $|r|$ >0.26, respectively (Scherrer, 1984).

CHAPTER III

DISSOLVED AND PARTICULATE MATERIAL LEVELS AND FLUXES AT THE RIVERS' OUTLETS

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1. Dissolved and particulate material levels at the rivers' outlets

The freshwater discharges varied greatly throughout the seasons and averaged 15.40 and 11.70 $m^3 s^{-1}$ at the MR and SR outlets, respectively (Fig. 16). The maximum water discharges occurred during November-April, and very low flows, which did not exceed 1 $m^3 s^{-1}$ on average, occurred during the rest of the year. During the wet period (October-April), the range of water salinities varied weakly for both rivers (0.1-1.4). The water salinity significantly increased in MR waters (10-33) during the dry and closing periods (May-September) but remained on the order of 1-2 PSS for SR waters (Fig. 16). MR had been closed from the sea for more than 6 months, from 12 June to 21 December 2014, and SR was nearly disconnected during three weeks in August. The two estuaries only delivered 0.84 10^9 m^3 of water into Annaba Bay as a result of the dry months over most of 2014.

The mean SPM level was 55 mg L^{-1} at the SR outlet and 61 mg L^{-1} at the MR outlet, with maxima in February for MR (190 mg L^{-1}) and March for SR (465 mg L^{-1}), which coincided with high river flows (Fig. 16). There were significant and large correlations between the SPM levels and the water flows (r =0.70 and r =0.69, for MR and SR, respectively: p <0.001) (Table 2, 3). The lower parts of the two estuaries were affected by marine intrusions during low river flows (<2 $m^3 s^{-1}$ for SR and during the closing period (0 $m^3 s^{-1}$) for MR).

At both rivers' outlets, all the nutrient forms varied greatly throughout the year, with usually high values of dissolved nutrients during the wet period, whereas particulate matter (Chl *a*, BSi, PON, POP, and POC) and dissolved organic nutrients (DON, DOP) increased during the dry period. This large variability was also shown by the one-way ANOVA (Table 1), with significant differences between sampling dates for both dissolved (except NO_2) and particulate matter in a given river. The Tukey HSD post hoc test showed that samples collected during the dry period were significantly different from those collected during the wet period.

All the dissolved nutrients concentrations were always higher in SR than MR. However, within the particulate organic matter pool, only the Chl *a* and PON

concentrations were more abundant in the SR waters, and the other particulate forms din not differ in both rivers' outlets.

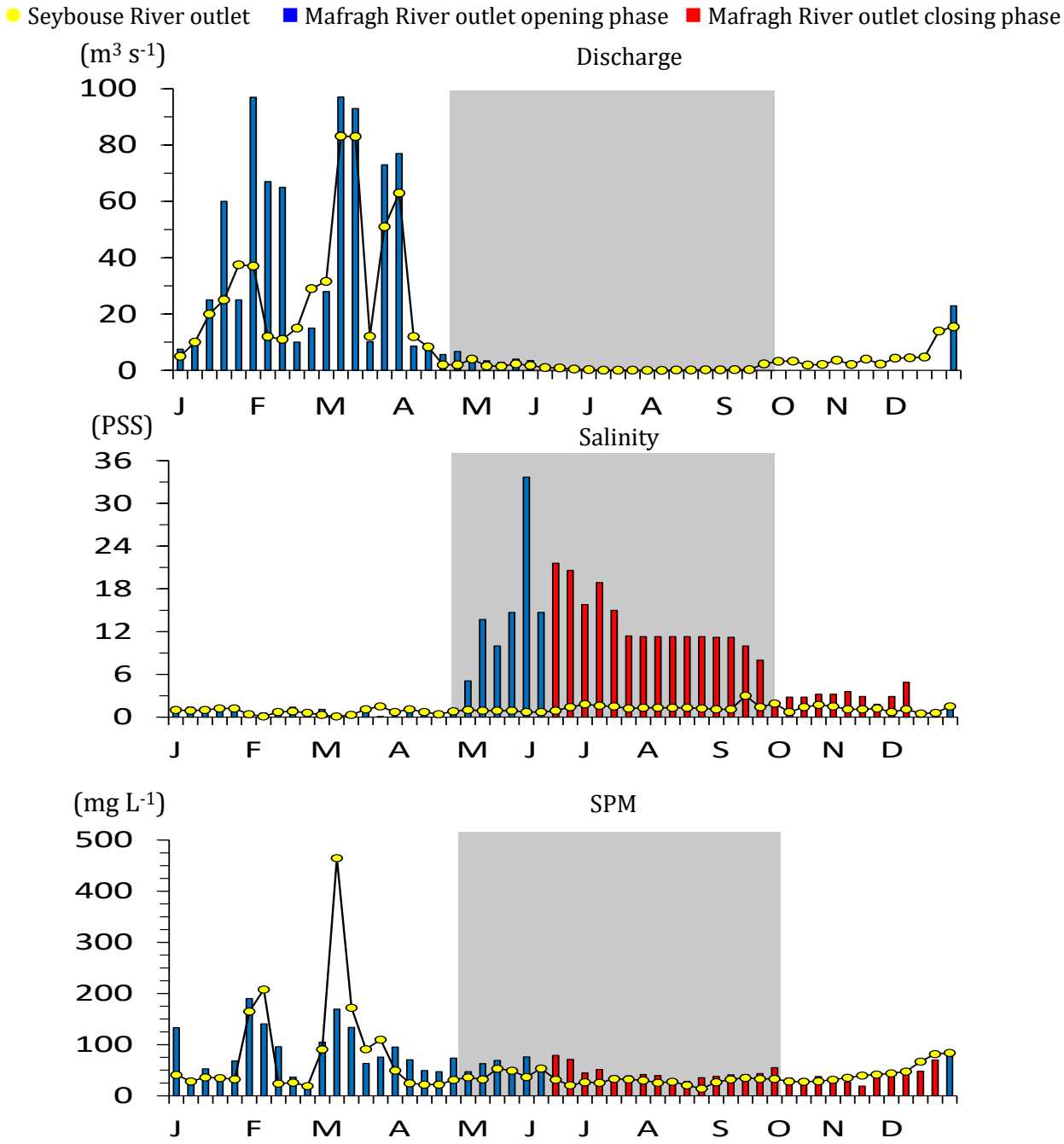

Figure 16. Seasonal variations in levels of discharge, salinity and suspended particulate matter (SPM) at the SR and MR outlets, during January-December 2014. The gray area represents the dry season.

The mean concentration of total nitrogen (TN) was 47 µmol L^{-1} at the MR outlet but increased to 98 µmol L^{-1} at the SR outlet (Fig. 18). Most of the TN was in the form of TDN. The NO_3 fraction represented one half and one third of the TDN in the MR and SR

waters, respectively. That oxidized nitrogen form was equal to that of the reduced form (NH_4) in SR but was two-fold higher in the MR waters.

The DON was nearly two times more abundant than PON at the MR outlet and 1.5-fold higher at the SR outlet (Fig 18). These two organic nitrogen forms exhibited the same variations and were largely and significantly correlated (r =0.82 at MR, and r =0.57 at SR; p <0.001) (Table 2, 3).

Table 1. One-way ANOVA results (F: Fisher test) showing variation factors between water flow and material concentrations in MR and SR from n =54 weekly samples in 2014; (ns: not significant; highly significant: p <0.001***).

	MR	SR
	F	F
Flow	5.16***	5.90***
SPM	3.14***	3.12***
Sal	29.45***	0.83^{ns}
NH_4	4.43***	13.63***
NO_2	1.69^{ns}	1.34^{ns}
NO_3	14.05***	13.06***
DIN	10.01***	8.33***
DON	14.76***	17.89***
TDN	11.12***	13.48***
PON	16.76***	9.22***
TN	11.76***	13.68***
$Si(OH)_4$	4.40***	6.67***
PO_4	10.73***	35.40***
DIP	8.31***	29.95***
DOP	32.41***	36.39***
TDP	23.80***	46.36***
POP	69.64***	25.95***
TP	63.71***	44.57***
BSi	7.80***	4.58***
Chl *a*	6.64***	16.53***
POC	7.80***	15.80***

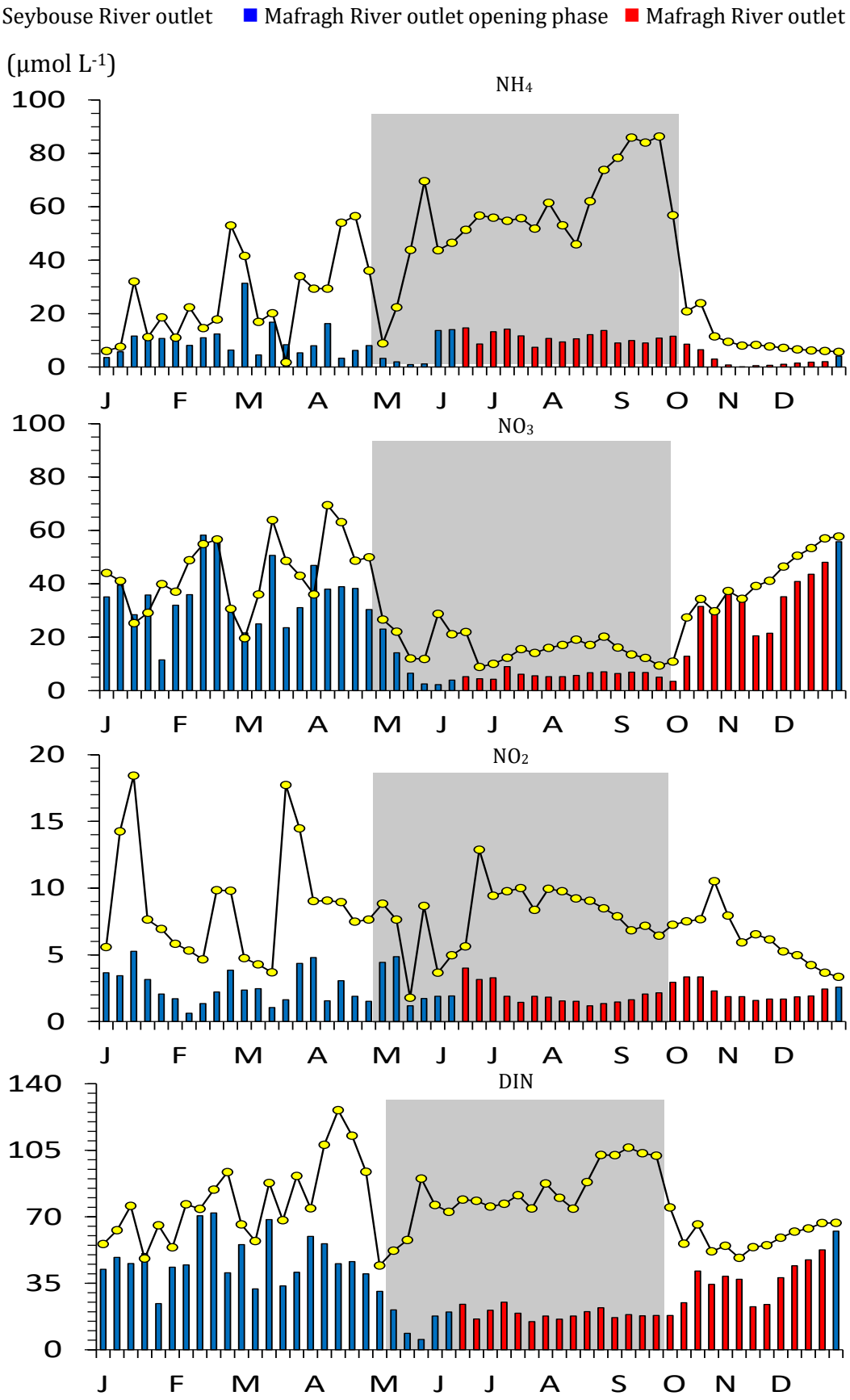

Figure 17. Seasonal variations in levels of dissolved forms of nitrogen, ammonium (NH_4), nitrate (NO_3), nitrite (NO_2) and dissolved inorganic nitrogen (DIN) at the SR and MR outlets, during January-December 2014. The gray area represents the dry season.

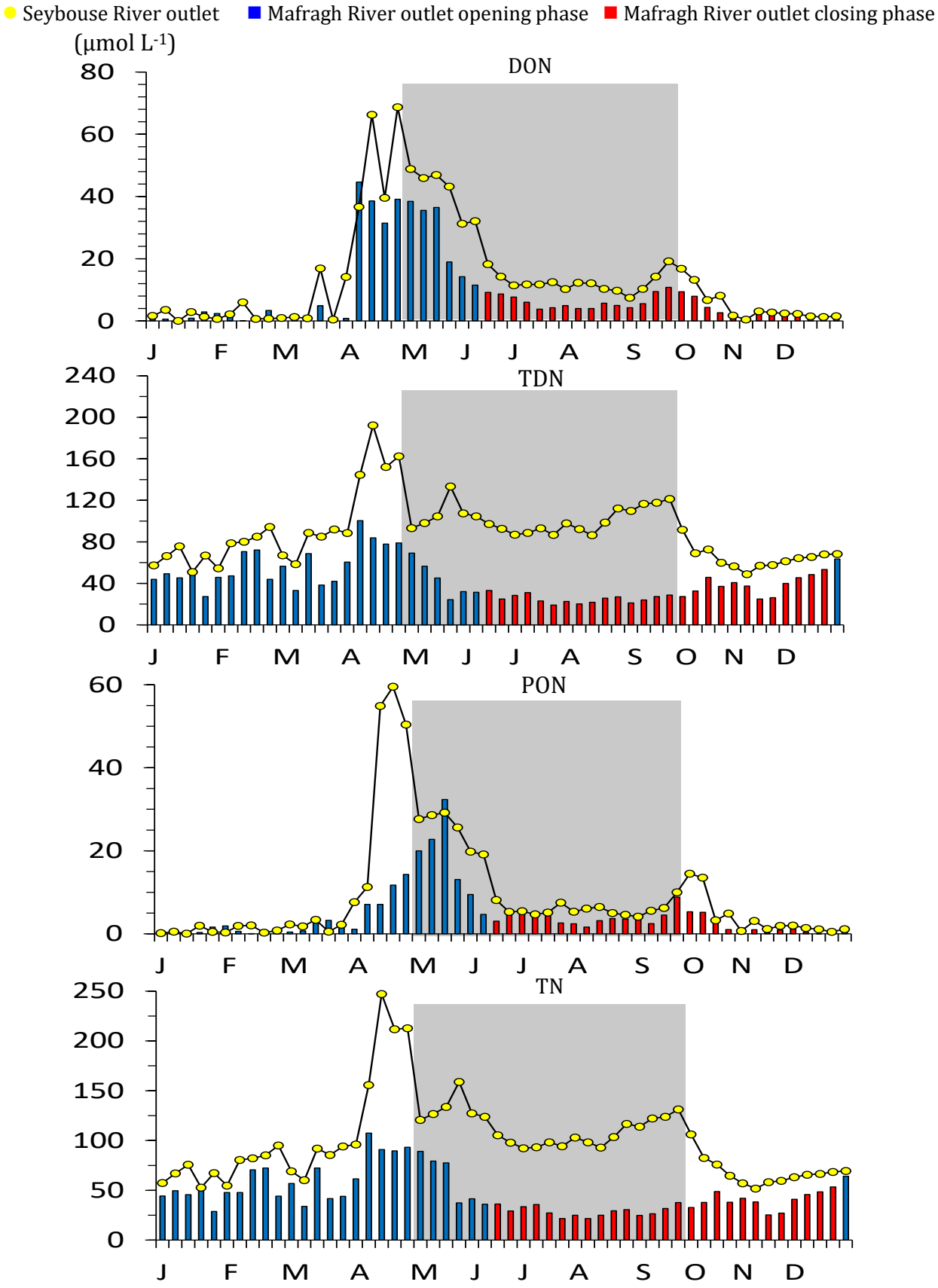

Figure 18. Seasonal variations in levels of dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), particulate organic nitrogen (PON) and total nitrogen (TN) at the SR and MR outlets, during January-December 2014. The gray area represents the dry season.

Table 2. Correlation matrix of the dissolved and particulate materials from Mafragh estuary during 2014.

	Salinity	SPM	Flow	NH_4	NO_2	NO_3	DIN	DON	TDN	PON	PO_4	DIP	DOP	TDP	POP	SiO_4	POC	BSi	Chl *a*
Salinity	1																		
SPM		1																	
Flow	**-0,42**	**0,77**	1																
NH_4				1															
NO_2					1														
NO_3	**-0,72**	0,27	**0,44**			1													
DIN	**-0,66**	0,34	**0,51**			**0,94**	1												
DON								1											
TDN	**-0,51**		0,29			**0,74**	**0,78**	**0,49**	1										
PON	0,28					-0,32	-0,37	**0,82**		1									
PO_4				0,32	-0,35	-0,39	-0,31		-0,30		1								
DIP				0,32	-0,31						**0,92**	1							
DOP	**0,65**		-0,30			**-0,62**	**-0,65**	0,40	-0,32	**0,67**			1						
TDP	**0,59**					**-0,66**	**-0,64**	0,38	-0,32	**0,56**	**0,62**	**0,53**	**0,86**	1					
POP	0,39		-0,32	-0,27		**-0,45**	**-0,54**	**0,49**		**0,77**			**0,82**	**0,64**	1				
SiO_4	**-0,56**	**0,50**	**0,62**			**0,59**	**0,65**		**0,44**	-0,39			**-0,47**	-0,35	**-0,42**	1			
POC	0,46	**-0,43**	**-0,57**		-0,30	**-0,66**	**-0,68**		**-0,62**		0,41		0,28	0,35		**-0,64**	1		
BSi	0,37					**-0,53**	**-0,52**		**-0,48**		**0,45**	0,26	0,34	0,42	0,27	-0,35	**0,44**	1	
Chl *a*		-0,36	-0,40			**-0,49**	**-0,50**		-0,36		**0,42**	0,27	0,34	**0,43**	0,26	**-0,47**	**0,64**	**0,55**	1

p =0.001***, $|r|$ >0.42
p =0.01**, 0.32<$|r|$ >0.42
p =0.05**, 0.26< r>0.32

Table 3. Correlation matrix of the dissolved and particulate materials from at Seybouse estuary during 2014.

	Salinity	SPM	Flow	NH_4	NO_2	NO_3	DIN	DON	TDN	PON	PO_4	DIP	DOP	TDP	POP	SiO_4	POC	BSi	Chl *a*
Salinity	1																		
SPM	-0,41	1																	
Flow	-0,40	**0,69**	1																
NH_4			-0,30	1															
NO_2					1														
NO_3	-0,34		0,35	**-0,67**		1													
DIN				**0,74**			1												
DON			-0,30	0,29				1											
TDN				**0,64**			**0,84**	**0,80**	1										
PON							0,38	**0.57**	**0,77**	1									
PO_4	**0,47**		-0,38	0,36		**-0,50**					1								
DIP	**0,44**	-0,27	-0,36	0,41		**-0,49**					**0,97**	1							
DOP			-0,34	**0,63**		**-0,68**		**0,43**	0,39	0,27	0,27	0,26	1						
TDP	0,33		**-0,43**	**0,68**		**-0,75**			0,29		**0,66**	**0,66**	**0,90**	1					
POP			**-0,43**	**0,52**		**-0,63**		**0,57**	0,40	**0,42**		0,30	**0,87**	**0,82**	1				
SiO_4	-0,29	**0,56**	**0,68**	-0,33		0,39		-0,31		-0,28	-0,37	-0,38	**-0,43**	**-0,51**	**-0,53**	1			
POC	**0,48**	-0,33	**-0,61**	0,35		**-0,48**					**0,72**	**0,67**	0,38	**0,61**	**0,56**	**-0,51**	1		
BSi	**0,47**			0,38		**-0,43**					**0,52**	**0,49**	**0,42**	**0,55**	0,36		**0,55**	1	
Chl *a*	**0,51**	-0,32	**-0,47**	**0,66**		**-0,65**	0,29		0,31		**0,62**	**0,59**	**0,68**	**0,80**	**0,82**	**-0,52**	**0,70**	**0,62**	1

p =0.001***, $|r|$ >0.42
p =0.01**, 0.32<$|r|$ >0.42
p =0.05**, 0.26< r>0.32

The DON concentrations followed a clear seasonal cycle in both rivers, with high values in the dry period that reached 20.70 and 11.90 µmol L^{-1} in SR and MR, respectively. The values during the wet period were half those during the dry period in the two rivers' outlets (Fig. 18).

The DIN concentrations increased during the high river flows (wet period), reaching 43.7 µmol L^{-1}, but dropped to 18.5 µmol L^{-1} in the MR waters during the dry period (Fig. 17). Unlike that for MR waters, large amounts of NH_4 were supplied during summer in SR waters (Fig. 17), which increased the DIN amount and fraction within the TN compounds. The NH_4 levels were, in fact, negatively correlated with SR flow (r =-0.30, p <0.05). Jointly with the increase in NH_4 level in the dry season (56 µmol L^{-1} in SR), the NO_3 level decreased 3-fold and 5.5-fold in SR and MR waters, respectively (Fig. 17). The oxidized nitrogen was largely supplied during wintertime and increased with river flow both in SR (r = 0.35, p <0.01) and MR (r =0.44, p <0.001) waters (Table 2, 3).

The two rivers showed high concentrations of total phosphorus (TP) throughout the seasons, in particular during the dry period (Fig. 20), when the dissolved organic (DOP) and particulate (POP) forms were supplied by the release and development of phytoplankton organisms. Those phosphorus organic forms were highly and significantly correlated with the chlorophyll *a* levels. The correlation coefficients of DOP-Chl *a* were r =0.82 (p <0.001) and 0.34 (p <0.01) for SR and MR, respectively, and the POP-Chl *a* correlation was 0.68 (p <0.001) for SR and only 0.26 (p<0.01) for MR (Table 2, 3). The TP concentrations were slightly elevated in SR (18.4 µmol L^{-1}on average) compared to that encountered in MR waters (13.2 µmol L^{-1}) but had the same seasonal cycle (Fig. 20). Within TP, the particulate form was dominant at 53% and 40% at the MR and SR outlets, respectively, and the dissolved organic form also constituted an important fraction (22%) at the two sites. Because DOP may have mainly originated from the degradation of POP, there were large correlations between the two forms in both rivers (r =0.80, p =0.001). The dissolved inorganic phosphorus (DIP) formed between approximately a third and a fourth of the TP amounts and evolved similarly over the seasons. The concentrations of phosphate (PO_4) were, however, more elevated in SR (4.90 µmol L^{-1}) than in MR (2.20 µmol L^{-1}) and increased during the dry season by approximately 36% over that in the wet season (Fig. 19).

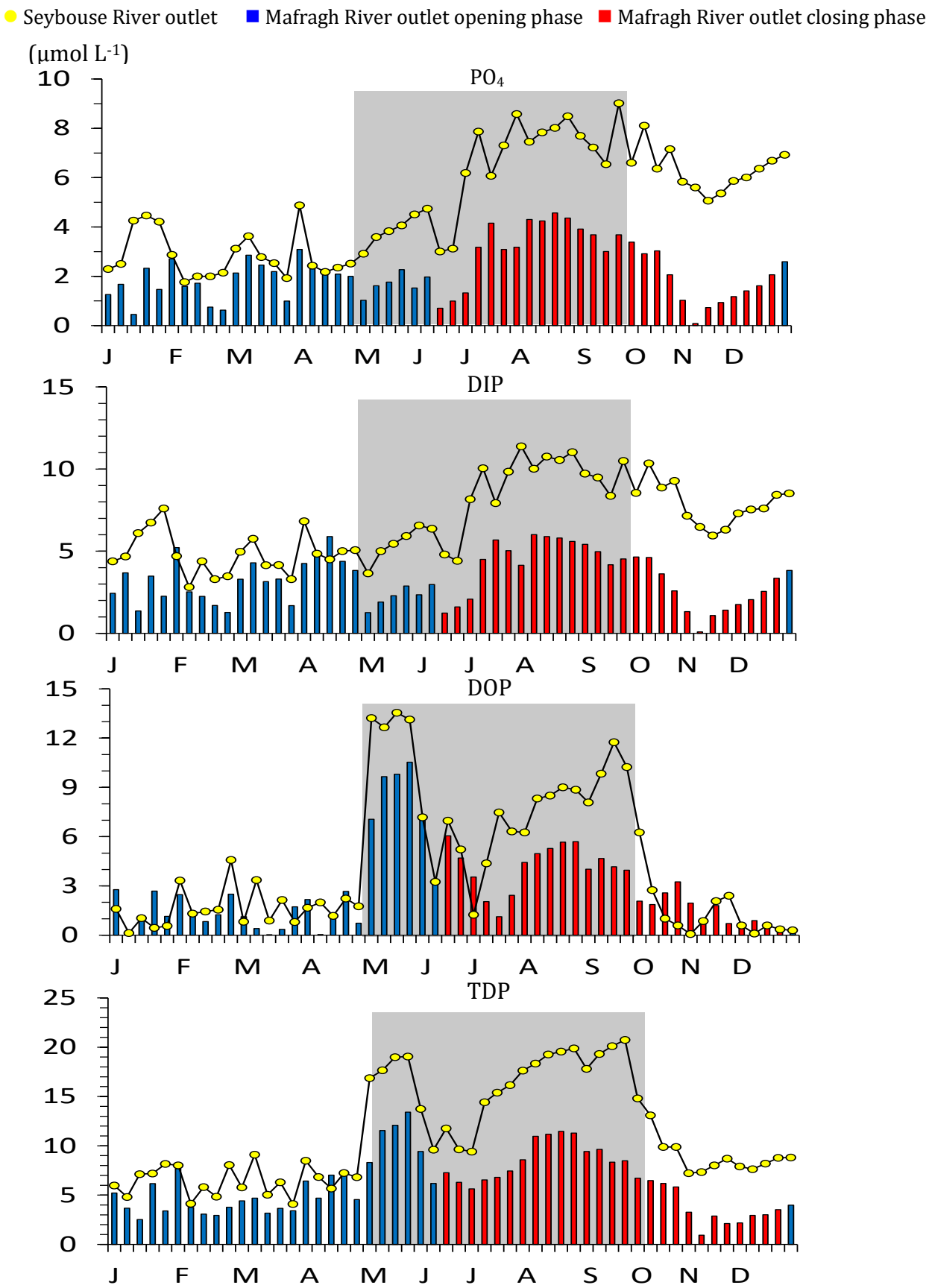

Figure 19. Seasonal variations in levels of phosphate (PO_4), dissolved inorganic phosphorus (DIP), dissolved organic phosphorus (DOP) and total dissolved phosphorus (TDP) at the SR and MR outlets, during January-December 2014. The gray area represents the dry season.

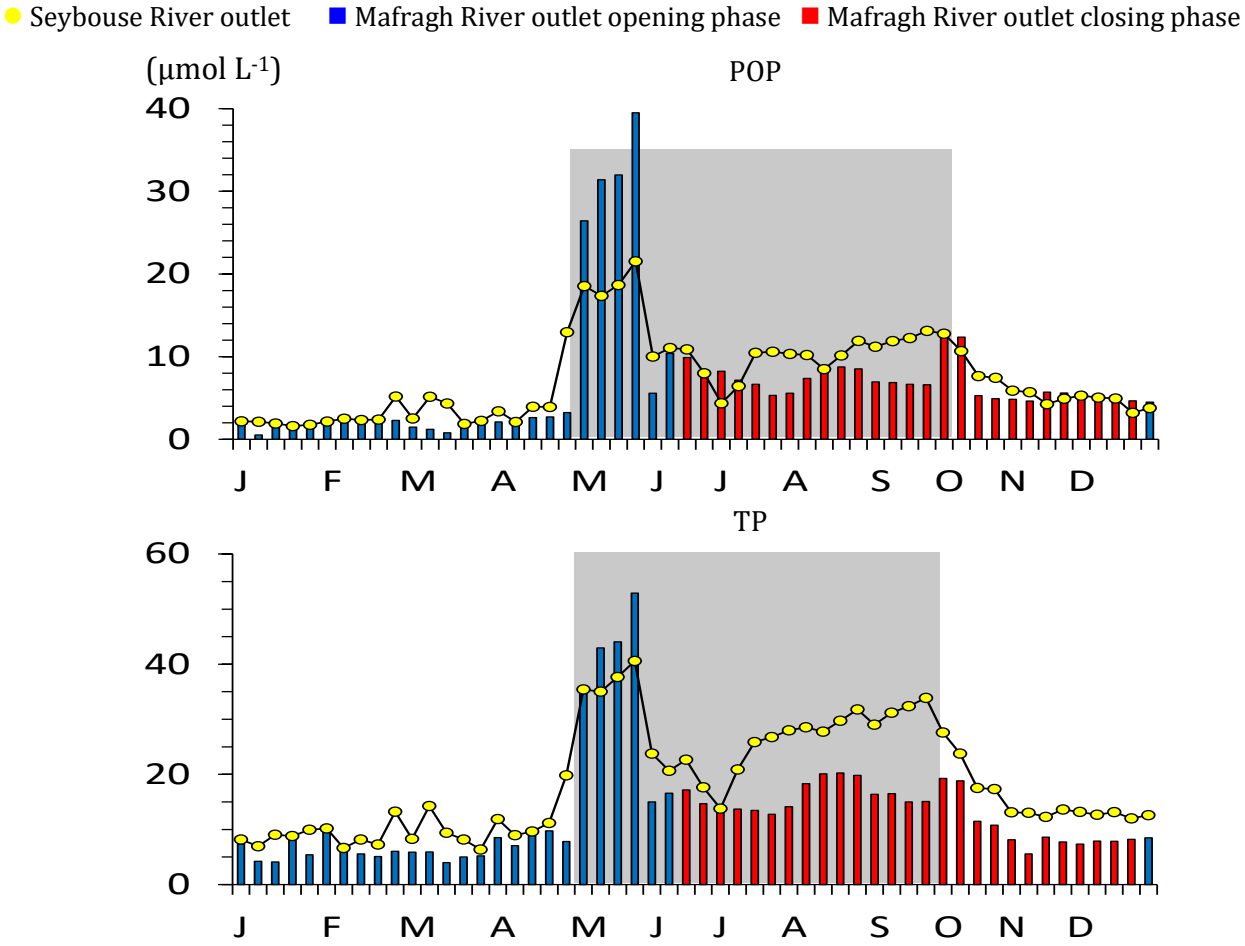

Figure 20. Seasonal variations in levels of particulate organic phosphorus (POP) and total phosphorus (TP) at the SR and MR outlets, during January-December 2014. The gray area represents the dry season.

At the SR outlet, although the DIN:PO_4 ratio (herein referred to as N:P) average value (19.50) did not deviate much from the standard Redfield ratio (78%of the samples had 8<N:P>30) but deviated greatly from the equilibrium situation (Fig. 22). In MR waters, however, half of the samples had 8<N:P>30, and 25 samples presented comparable values to the Redfield standard ratio. Most of the deviated Redfield values at both rivers' outlets occurred during the dry period.

The mean total silica (TSi) levels were 77 µmol L^{-1} and 90 µmol L^{-1} at the MR and SR outlets, respectively, where the contributions of dissolved silica (SiO_4) exceeded 55%. The levels of SiO_4 were generally low in both estuaries and averaged 41 µmol L^{-1} in MR and 51 µmol L^{-1} in SR, but during the wet season, the amounts increased with the river water flows (Fig. 21). There were high SiO_4-discharge correlations: r =0.62 and 0.68 in SR and MR, respectively (p <0.001) (Table 2, 3). At the SR outlet, the SiO_4:DIN ratio (herein referred to as Si:N) was often low (Si:N <1 in 76% of samples), with an average

value that did not exceed 0.72 (Fig. 22). The Si:N ratio was, however, more elevated in MR waters (1.40), and only 24% of the samples had values <1. For N:P, most of the low and unbalanced Si:N values occurred during the dry period at the SR outlet (Fig. 22).

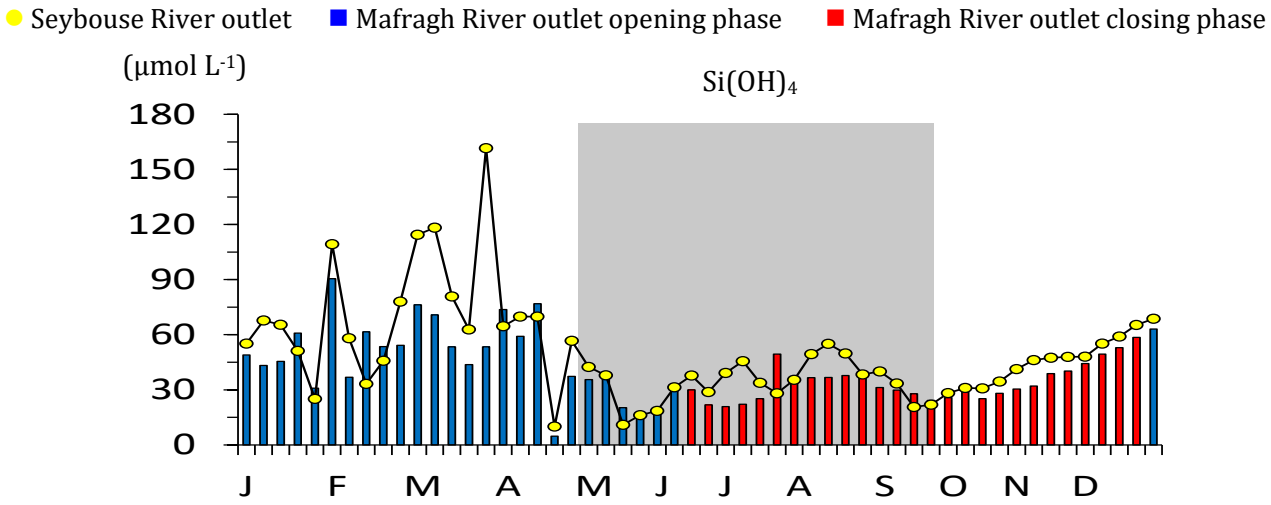

Figure 21. Seasonal variations in silica ($Si(OH_4)$) at the SR and MR outlets, during January-December 2014. The gray area represents the dry season.

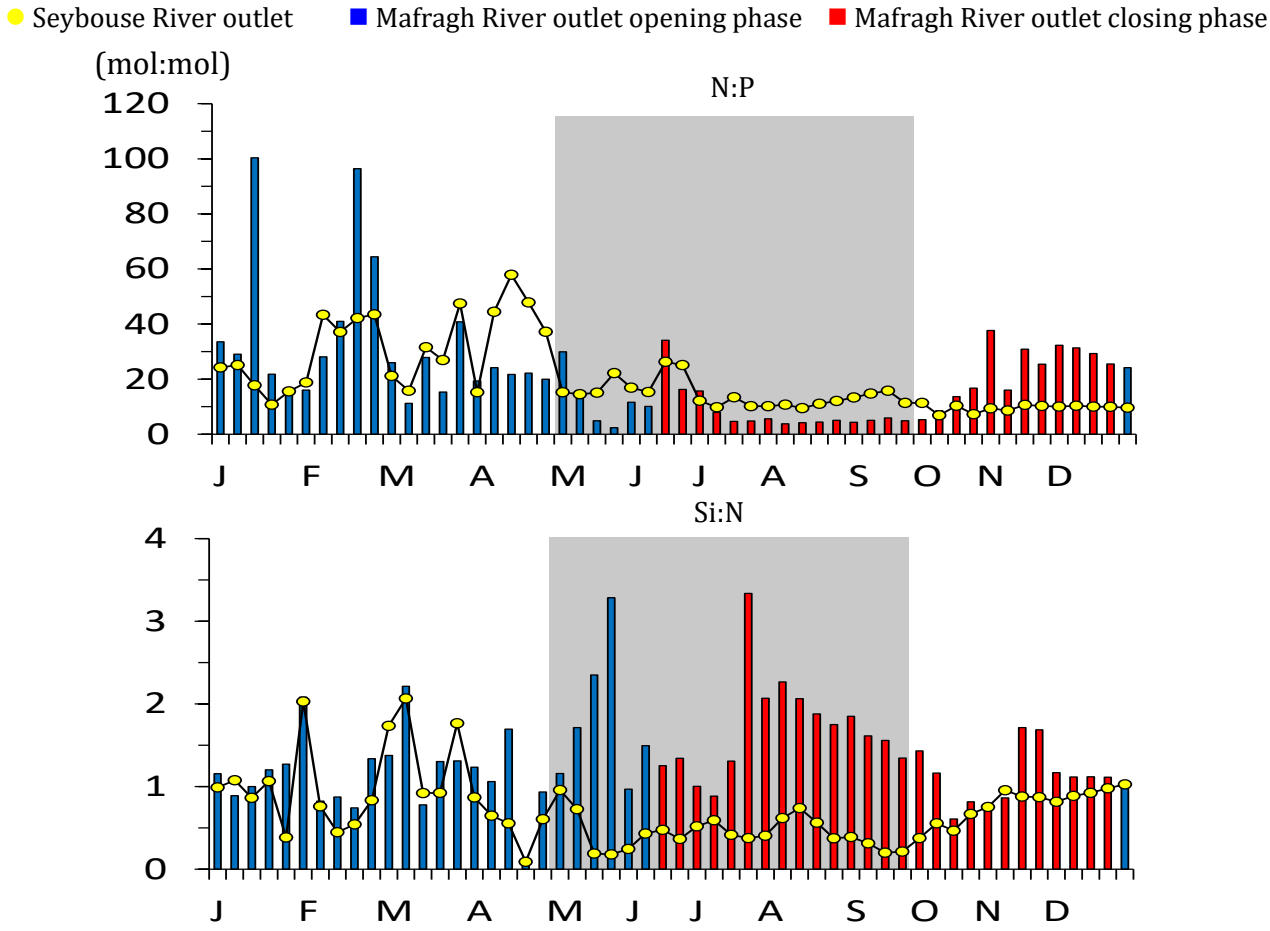

Figure 22. Si:N ($Si(OH_4)$:DIN); N:P (DIN:PO_4) molar ratios at the Mafragh and Seybouse River outlets during 2014. The gray area represents the dry season.

Similar to particulate nitrogen and phosphorus, particulate silica (BSi) displayed a clear seasonal cycle, with exceptionally high values during the dry period that reached 1.42 mg L^{-1} and 1.36 mg L^{-1} (1 mg Si-SiO_2 = 35.71 µmol Si-SiO_2) at the SR and MR outlets, respectively (Fig. 23).

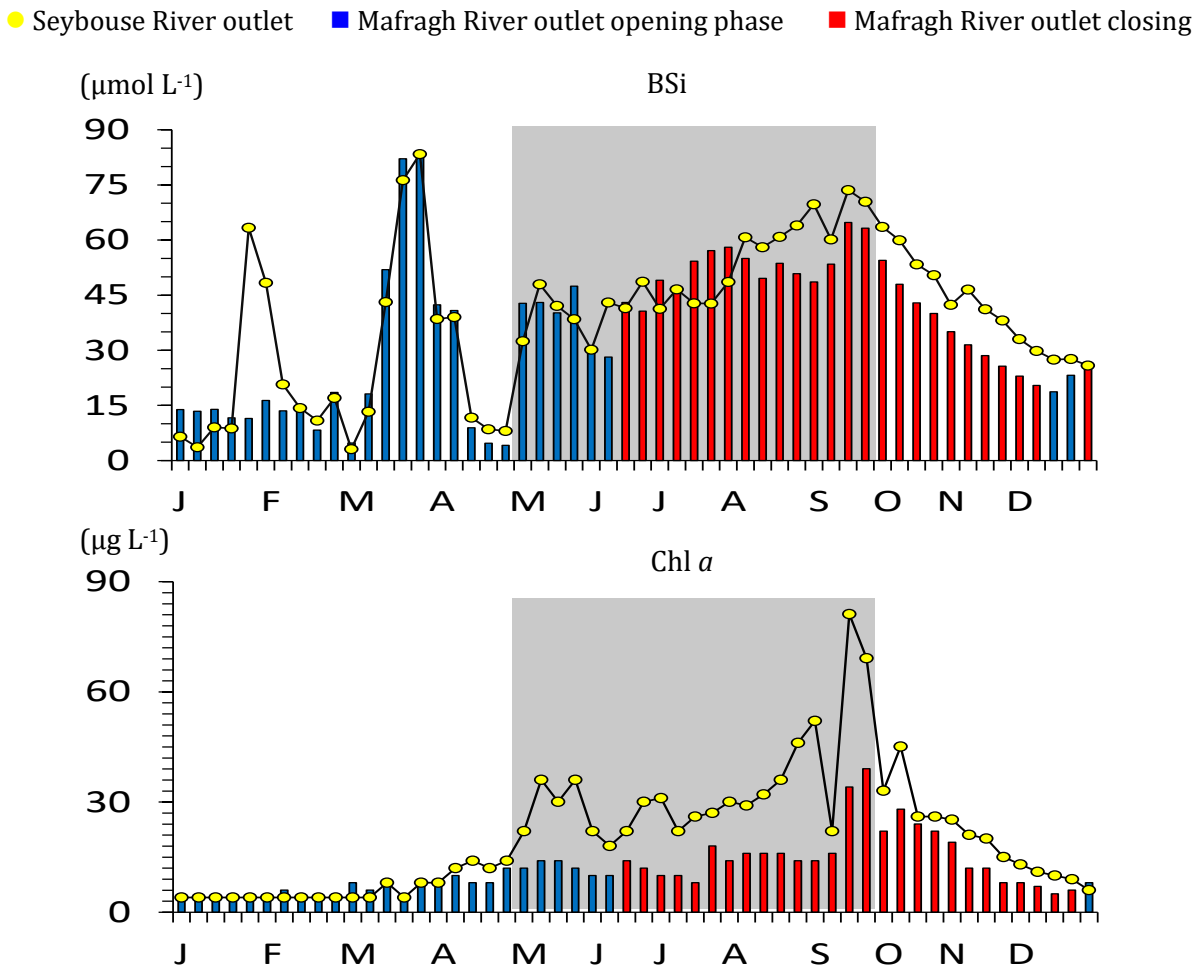

Figure 23. Seasonal variations in levels of biogenic silica (BSi) and chlorophyll (chl *a*) at the Mafragh and Seybouse River outlets during 2014. The gray area represents the dry season. The gray area represents the dry season.

Overall, the BSi concentrations were found to be remarkably elevated throughout the year, even in winter, which was generally the lowest productive period of the year. In addition, it can be noted that the BSi concentrations were largely comparable to the dissolved inorganic form values, and the ratio SiO_4:BSi was not much different from unity (1.10 and 1.25 in MR and SR waters, respectively). Nearly half of the available dissolved silica would be converted in the form of particulate silica as diatoms frustules. There were in fact significant correlations between the Chl *a* and BSi concentrations in the two rivers' waters (r =0.55 and 0.62 for SR and MR, respectively; p <0.001) (Table 2,

3). The SiO_4 amounts however were negatively correlated (r =-0.35, p =0.01) with BSi due to their opposite seasonal cycles in MR waters, but that correlation became positive in the dry period for the SR waters. Although the ratio Si:N did not exceed unity in most cases in both rivers, the ratio of the organic form BSi:PON displayed elevated values of approximately 27 and 20 in the SR and MR waters, respectively.

The two rivers showed high Chlorophyll *a* amounts, particularly during the warm and dry period (34 and 15 µg L^{-1} for SR and MR, respectively) (Fig. 23). The phytoplankton biomasses peaked in May and September, consecutive to the decline in river flow (SR) or during the closing period (MR) and to the high NH_4 and PO_4 loads during summertime, as previously described. The SR waters always experienced more elevated Chl *a* concentrations, which averaged 21 µg L^{-1}, in comparison to those of MR, which were approximately 12 µg L^{-1}.

Diatom populations may have represented 10% of the total phytoplankton community because the ratio BSi:Chl *a* was generally approximately 0.1 in MR and 0.05-0.11 in SR (Fig. 25). During the dry period, diatoms may have represented only 5% (BSi:Chl *a* = 0.05) of the community in SR waters. Unlike the phytoplankton biomasses, the values of POC were comparable (10 mg L^{-1}) in both estuaries and had the same seasonal variation, with maximum values during the dry period (Fig. 24). The POC levels had large and significant correlations with the phytoplankton biomasses (r =0.64 and 0.70 for MR and SR waters, respectively; p <0.001).

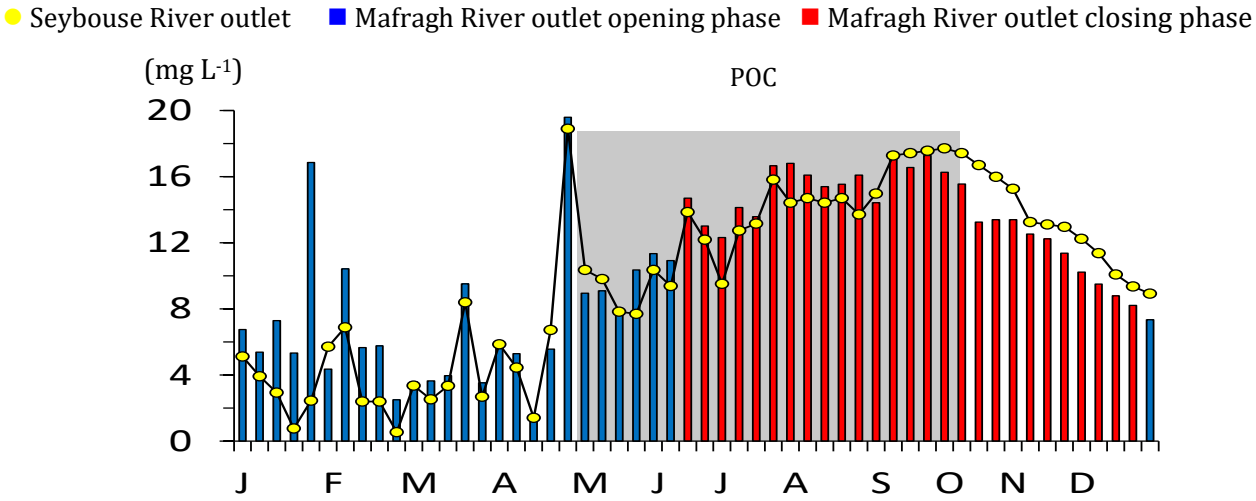

Figure 24. Seasonal variations in levels of particulate organic carbon (POC) at the SR and MR outlets, during January-December 2014. The gray area represents the dry season.

In addition, the POC:Chl *a* ratios displayed very high values in both estuaries and varied from 100-2100, with averages of 648 at SR and 1089 at MR. Those exceptionally high values may have been related to the advanced rates of phytoplankton standing stock degradation in such highly dynamic systems. The minimum POC:Chl *a* value occurred during the blooming period. The BSi was, on average, between 10-18.8% of the POC concentration, and its fraction increased in the wet period, particularly at the SR outlet. This may mean that diatoms constituted an important fraction of the total particulate carbon. In addition, POC was a main component of SPM, representing 32-45% in the dry period and approximately 20% in the wet period and with a maximum POC:SPM ratio observed during the blooming period (Fig. 25).

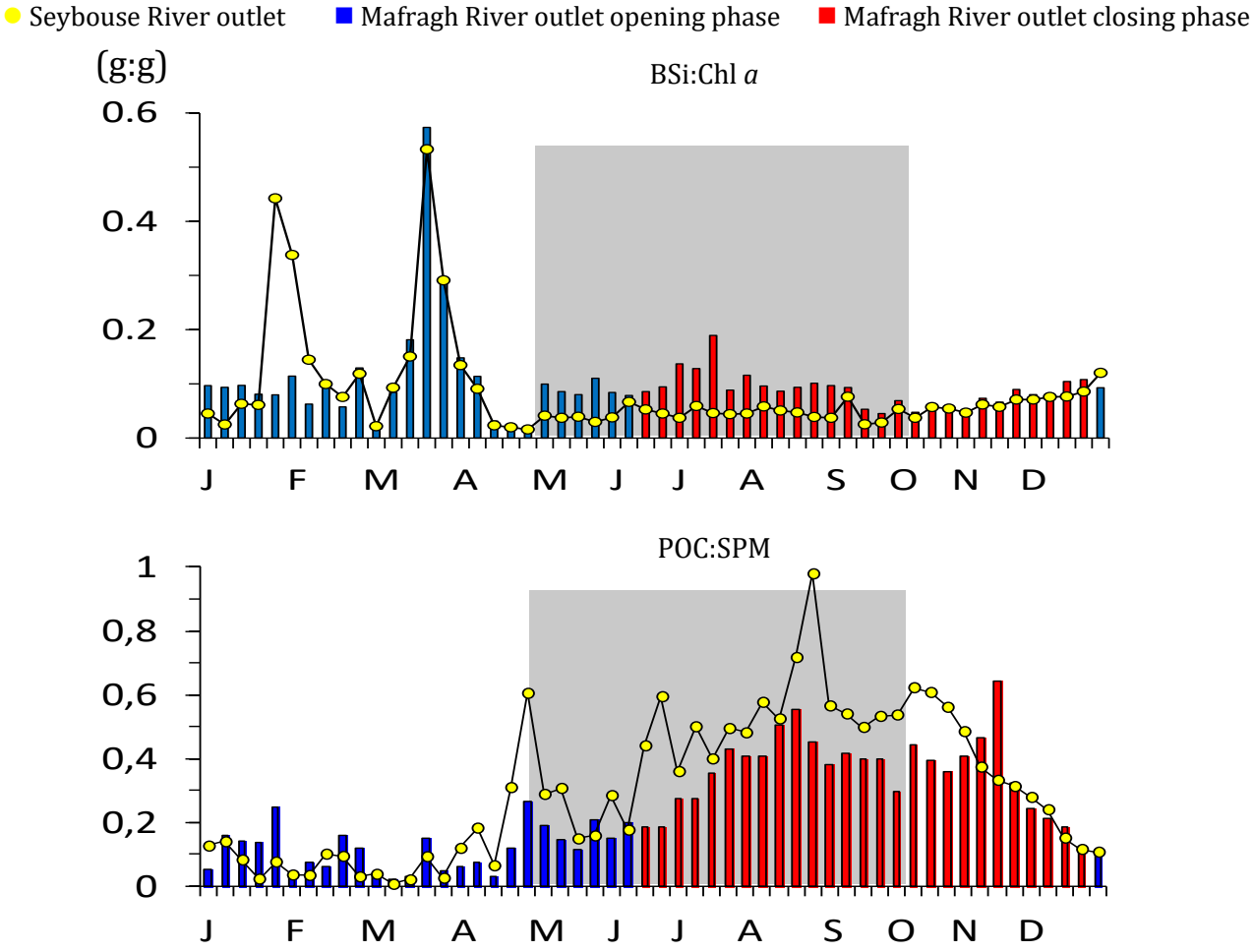

Figure 25. BSi:Chl *a* and POC:SPM ratios at the Mafragh and Seybouse River outlets during 2014. The gray area represents the dry season. The gray area represents the dry season.

Because the rivers' outlets are highly productive, particulate organic matter constituted a relevant fraction of SPM. However, there was a negative correlation between POC and SPM (r =-0.33 and p <0.01 in SR, and r =-0.43 and p <0.001 in MR) and between POC and

water flow (r =-0.61 and p <0.001 in SR, and r =-0.57 and p <0.001in MR) (Table 2, 3). This was because river flow and SPM increased during the wet period in contrast to POC, which was mainly produced during the dry period.

2. *Dissolved and particulate material fluxes at the rivers' outlets*

Together, MR and SR delivered 762 10^3 kg yr^{-1} of TN during 2014, of which TDN contributed 95.76% (Table 4). The DIN was the major component of TDN for both Mafragh and Seybouse rivers outlets when compared to the DON fraction (Table 4).

Within the DIN form, $N\text{-}NO_3$ was the major component in the riverine inputs (65.7%). That oxidized nitrogen form dominated (67.7%) the TN mass delivered from the MR outlet. However, the $N\text{-}NH_4$ flux was 2.5-fold the $N\text{-}NO_3$ flux in the MR and SR inputs, contributing with 188 10^3 kg yr^{-1} (Table 4).

SR and MR delivered together 237.4 10^3 kg yr^{-1} of TP (Table 4), from which the TDP constituted an important fraction (65.8%). The Bay of Annaba received 112 10^3 kg yr^{-1} of DIP, and the two rivers contributed nearly equally to both $P\text{-}PO_4$ and DOP inputs (Table 2).

Opposite that of PON, POP represented the major fraction within TP components (Table 4), contributing 34.2% on average. MR and SR delivered 2413 10^3 kg yr^{-1} of total silica (TSi), of which 68.9% was in the form of dissolved silica ($Si\text{-}SiO_4$), and delivered 750 10^3 kg yr^{-1} of particulate biogenic silica (Si-Bsi). Similar to particulate biogenic silica, the two rivers discharged large amounts of POC (4482 10^3 kg yr^{-1}), and MR extrusions formed 62.5% of the annual POC input. The BSi:POC loading ratio was approximately 0.1-0.2, depending on the river.

The rivers delivered important and approximately equal phytoplankton biomasses (5.8 10^3 kg yr^{-1} in total) into Annaba Bay. At the riverine outlets, the sediment yields were not elevated (7.5 and 16.7 10^3 kg SPM km^{-2} yr^{-1} for SR and MR, respectively). Not only did the lower catchments act as sedimentary basins, trapping sediments, but the many dry months of 2014 also most probably contributed to the reductions in sediment discharges. 3.4-5.2% of the SPM flux was in the form of POC (Table 4).

Table 4. Annual fluxes (kg yr^{-1} and mol yr^{-1}) of various dissolved and particulate materials from riverine and atmospheric sources estimated for 2014. Specific fluxes (kg km^{-2} yr^{-1}) are given between parentheses.

	Rivers					
	SR		MR		SR+MR	
	10^3 kg	mol yr^{-1}	10^3 kg yr^{-1}	mol yr^{-1}	10^3	mol yr^{-1}
NH_4	121 (18.6)	8641	66.7 (20.8)	4763	187.7	13404
NO_2	38.8 (6)	2771	17.1 (5.3)	1221	55.9	3992
NO_3	217 (33.4)	15498	249.8 (78.0)	17840	467	33338
DIN	377 (58.6)	26926	333.5 (104.2)	23818	711	50744
DON	29.9 (4.6)	2136	21.8 (6.8)	1557	51.7	3639
TDN	407 (62.6)	29068	355.4 (111.1)	25383	762.6	54451
PON	21.1 (3.2)	1507	13.4 (4.2)	957	34.5	2464
TN	428 (65.9)	35068	368.8 (115.2)	26339	797	61407
PO_4	40.9 (6.3)	1319	31.9 (10.0)	1029	72.8	2348
P_2O_5	21.1 (3.2)	680	18.2 (5.7)	587	39.3	1267
DIP	62 (9.5)	2000	50.1 (15.7)	1616	112,1	3616
DOP	21.9 (3.4)	706	22.3 (6.9)	718	44.2	1424
TDP	83.9 (12.9)	2706	72.4 (22.6)	2303	156.2	5009
POP	43.7 (6.7)	1409	37.4 (11.7)	1206	81.1	2615
TP	127.6 (19.6)	4115	109.8 (34.3)	3541	237.4	7656
$Si(OH)_4$	840 (129.4)	29996	823 (257.2)	29389	1663	59385
BSi	355.4 (54.7)	12691	394 (123.2	14070	749.6	26761
TaSi	1195 (183)	41602	1217 (380)	43459	2413	85061
POC	1679 (258.4)	148306	2802 (875.7)	233490	4482	381796
Chl *a*	2.8 (0.4)	3.11	3 (0.9)	3.33	5.8	6.44
SPM	48962 (75000)		53433 (167000)		102395	

3. Disscussion

3.1. Water and sediment deliveries

The main objective of this work is to assess the relative contributions of riverine and wet atmospheric inputs of materials into the Annaba area during the relatively dry year of 2014.

During the year of 2014, the MR and SR catchment' outlets together introduced nearly 0.84 X 10^9 m^3 of freshwater into the Annaba Bay (Table 5). This discharge represented about 15% of the annual rainfall corresponding to a specific flow of 86 mm. It is half the average value reported by UNEP/MAP (2013) and up to third that of Ounissi et al. (2016) (Table 5).

Table 5. Volume water discharge (10^9 m^3) delivered by some selected Mediterranean rivers.

Rivers	V X 10^9 m^3	Source
Ebro, Spain	13.66	UNEP/MAP, 2013
Rhone, France	53.52	UNEP/MAP, 2013
Pô, Italy	47.25	UNEP/MAP, 2013
Asi, Turkey	1.2	UNEP/MAP, 2013
Axios, Greece	3.24	UNEP/MAP, 2013
Meric, Turkey	7	UNEP/MAP, 2013
Kebir Rhumel, Algeria	0.99	Ounissi and Bouchareb, 2013
Kebir West, Algeria	0.76	Ounissi and Bouchareb, 2013
Saf-Saf, Algeria	0.82	Ounissi and Bouchareb, 2013
Mafragh, Algeria	0.20	UNEP/MAP, 2013
Seybouse, Algeria	0.38-1.17	Ounissi et al., 2016
Mafragh, Algeria	0.83-1.1	Ounissi et al., 2016
Mafragh, Algeria	2.05	Taamalah et al., 2016
Seybouse, Algeria	0.68	Aounallah, 2015
Mafragh, Algeria	0.47	This study
Seybouse, Algeria	0.37	This study

The long dry period from April to November 2014 also resulted in the strong lowering of the SR flow, which was not, however, lower than the minimum annual average value reported by UNEP/MAP (2013) and Ounissi et al. (2016). Whatever the hydrological conditions, the MR discharge was much more elevated compared to the SR one (e.g. Ounissi et al., 2014; Ounissi et al., 2016; Taamallah et al., 2016) (Table 5). Even if the MR has found the sea only for 6 months, it has contributed to more than half to the annual discharge into the Bay. Regarding its specific flow and discharge (e.g. Laborde et al., 2010; UNEP/MAP, 2013; Ounissi et al., 2014, 2016; Taamallah et al., 2016), the MR can be considered as the most important river in Algeria.

Not only the smaller river flows during 2014 significantly reduced the sediment loads (75 and 167 t km^{-2} yr^{-1} for Mafragh and Seybouse respectively), but dams probably trapped more than 70% of the incoming sediment masses, as observed in many contiguous Algerian river catchments (Ounissi and Bouchareb, 2013; Taamallah et al., 2016; Youcef and Amira, 2017) and Mediterranean (Table 6). Indeed, the rivers discharge only represented approximately 15% of the annual rainfall. For Mediterranean catchments, Sadaoui et al. (2017) reported sediment retention of 35%, corresponding to an anthropogenic sediment loss of 137 t km^{-2} yr^{-1}.

Table 6. Specific flux (t km^{-2} yr^{-1}) of suspended sediment (SPM) in some selected Mediterranean rivers.

Rivers	Flux	Source
North African catchments	800	Fox et al., 1997
Rhone, France	324	Pont et al., 2002
Mediterranean rivers	251	UNEP/MAP, 2003
Ebro, Spain	214	UNEP/MAP, 2003
Italian Rivers	780	UNEP/MAP, 2003
Medjerda, Tunisia	963	UNEP/MAP, 2003
Moulouya, Morocco	250	UNEP/MAP, 2003
Kebir Rhumel, Algeria	64	Ounissi and Bouchareb, 2013
Kebir West, Algeria	374	Ounissi and Bouchareb, 2013
Saf-Saf, Algeria	192	Ounissi and Bouchareb, 2013
Seybouse, Algeria	20	Aounallah, 2015
Mafragh, Algeria	1974	Taamalah et al., 2016
Soummam, Algeria	28	Youcef and Amira, 2017
Isser, Algeria	52	Youcef and Amira, 2017
Sebaou, Algeria	59	Youcef and Amira, 2017
Mafragh, Algeria	167	This study
Seybouse, Algeria	75	This study

3.2. Dissloved nutrients level and delivery

Despite the low water and sediment yields characterizing the year 2014, dissolved inorganic nutrient of human activities origin (NH_4 and PO_4) displayed large concentrations during the dry season, but both $Si(OH)_4$, which is mainly of natural origin and NO_3 levels largely decreased. Concentrations of NO_3 and $Si(OH)_4$ remained not elevated even during the wet season, because of the reduced water flow. It appears that by dry hydrological conditions, the anthropogenic impact is more expressed and can overwhelm the nutrient loading of water compared to the natural chemical action.

Compared to the mean world river' basins value (Table 7), levels of $Si(OH)_4$ in MR and SR are 3.5-fold lower. Not only this impoverishment is due to the reservoirs retention (Meybeck and Vörösmarty 2005; Humborg et al., 2006; Avilés and Niell, 2007; Ounissi and Bouchareb, 2013) but also the estuarine part buffering can be relevant (Canton et al., 2012; Hallas and Huettel, 2013).

Table 7. Silicic acid $Si(OH)_4$ concentrations (µmol L^{-1}) in some selected Mediterranean rivers and other rivers.

Rivers	$Si(OH)_4$	Source
Mean world concentration	150	Conley, 1997
Amazon, Brazil	138	Conley, 1997
Mississippi, US	97.7	Conley, 1997
Danube, Germany	55	Conley, 1997
Rhone, France	67	Moutin et al., 1998
Mean world concentration	150	Humborg, 2000
Ebro, Spain	50	Cruzado et al., 2002
Nile, Egypt	52	Shehata and Badr, 2010
Pô, Italy	26	Viaroli et al., 2013
Kebir West, Algeria	77	Ounissi and Bouchareb, 2013
Kebir Rhumel, Algeria	55	Ounissi and Bouchareb, 2013
Saf-Saf, Algeria	96	Ounissi and Bouchareb, 2013
Seybouse, Algeria	73	Ounissi el al., 2014
Mafragh, Algeria	53	Ounissi el al., 2014
Mafragh, Algeria	41.08	This study
Seybouse, Algeria	50.28	This study

In contrast, PO_4 and NH_4 concentrations at SR in particular remain elevated compared to the major Mediterranean rivers (Table 8), where these nutrients are decreasing (Ludwig et al., 2010; UNEP/MAP, 2013) (Table 8). Nevertheless, the wastewater treatment plant recently implanted in 2010 had sensibly lowered NH_4 concentrations in SR waters, which were decreased by 6-fold (see Ounissi et al., 2014) (Table 8). Although this large reduction in NH_4 supply, the SR water remains however disturbed as the N:P molar ratio was unbalanced in 78% of samples. This disturbance is more expressed through the very low values of Si:N, which were mostly <1. Not only the DIN levels increased in most Mediterranean rivers (Ludwig et al., 2010) but also the silicon concentrations have markedly decreased owing to silicon retention behind dams (Table 7).

Table 8. Dissolved nutrients concentrations (µmol L^{-1}) in some selected Mediterranean rivers.

Rivers	NO_3	NH_4	DIN	DON	DIP	POD	Source
Asi, Turkey	205.3	10.04	215.7		3.33		Tepe et al., 2005
Medjerda, Tunisia	32						Bouraoui et al., 2005
Asi, Turkey	205.3	10.04	215.7		3.33		Tepe et al., 2005
Moulouya, Morocco	29		50				Makhoukh et al., 2011
Nile, Egypt	119.05						UNEP/MAP, 2013
Rhone, France	24.08	3.91	28.43		0.54		UNEP/MAP, 2013
Ebro, Spain	39.59	3.91	44.17	21.43	0.65		UNEP/MAP, 2013
Pô, Italy	37.98	5.02	43.67	142.2	0.75		UNEP/MAP, 2013
Evros, Greece	18.75	31.25	53.34		5.16		UNEP/MAP, 2013
Menderes, Turkey	6.79	26.23	33.46		1.08		UNEP/MAP, 2013
Axios, Greece	31.67	7.81	41.94		5.81		UNEP/MAP, 2013
Kebir Rhumel, Algeria	13	1	15	36	2	14	Ounissi and Bouchareb, 2013
Kebir West, Algeria	32	9	39	18	5	10	Ounissi and Bouchareb, 2013
Saf-Saf, Algeria	12	26	44	15	8	4	Ounissi and Bouchareb, 2013
Seybouse, Algeria	30	180	220		3.6		Ounissi et al., 2014
Mafragh, Algeria	8	8	26		1.3		Ounissi et al., 2014
Mafragh, Algeria	23.41	8.17	33.95	8,6	3.3	2.85	This study
Seybouse, Algeria	32.42	34.92	75.17	14.09	6.83	4.19	This study

The river flow lowering during most of 2014 has resulted in very low fluxes of all dissolved nutrients. Together SR and MR catchments delivered 710 X 10^3 kg yr^{-1} of DIN (or 73 kg km^{-2} yr^{-1}); 73 10^3 kg yr^{-1} of $P\text{-}PO_4$ (or 8 kg km^{-2} yr^{-1}) and 1660 X 10^3 kg yr^{-1} of $Si\text{-}Si(OH)_4$ (171 kg km^{-2} yr^{-1}). These loads are very low compared to those of Mediterranean rivers (El Boukhary 2005; Ludwig et al., 2009; UNEP/MAP, 2013) and Algerian rivers (Ounissi and Bouchareb, 2013; Ounissi et al., 2014) (Table 9).

In addition, the dissolved inorganic nutrient deliveries from SR and MR catchments (Ounissi et al., 2014) were found to be 2.5-6 higher by wet years than those of dry years like 2014. Most importantly is the dominance of the MR fluxes of all dissolved nutrients, compared to that of SR, which is usually considered as the most developed catchment (Ounissi et al., 2014). Yet, the strong NH_4 level and flux, which characterize SR waters, markedly declined. In 2014, the flux of this reduced nitrogen form decreased by nearly 4-fold compared to values of 2007-2009 reported by Ounissi et al. (2014).

The lowering of both $Si(OH)_4$ concentrations and Si:N ratio in SR waters and in a lesser degree in MR waters have resulted in the lowering of diatoms fraction (BSi:Chl *a*: nearly 0.10) within phytoplankton communities. Additionally, the elevated Chl *a* biomass at SR outlet may be linked to the non-siliceous and harmful phytoplankton taxa

development. In contrast to SR, MR appears to function as a near-pristine hydrosystem, with low nutrient supply and more balanced Redfield ratios, as has been previously reported (Khélifi-Touhami et al., 2006; Ounissi et al., 2014; Ounissi et al., 2016).

Table 9. Specific fluxes (kg km^{-2} yr^{-1}) of nutrients from some selected Mediterranean coastal rivers.

Rivers	NH_4	NO_3	DIN	DON	PO_4	$Si(OH)_4$	References
Axios, Greece			952		665.2	1972	El Boukhary, 2005
Aliakmon, Greece			782		106.2	2638	El Boukhary, 2005
Gallikos, Greece			850		37	2550	El Boukhary, 2005
Pinios, Greece			1163		175	3489	El Boukhary, 2005
Ebro, Spain	4.4	146	152.7		2	140	Falco et al., 2010
Pinios, Greece	180	496	700		166		UNEP/MAP, 2013
Têt, France	383	331	756	184	34		UNEP/MAP, 2013
Ter, Spain	24.3	314	350	41.9	15.4		UNEP/MAP, 2013
Adige, Italy	39.7	556	605	159	24.8		UNEP/MAP, 2013
Pô, Italy	58.2	1520	1590	1290	45.2		UNEP/MAP, 2013
Rhone, France	38.4	816	866		27.4		UNEP/MAP, 2013
Reno, Italy	91.5	385	486	187	19.3		UNEP/MAP, 2013
Argens, France	11.3	213	230	88.7	11.3		UNEP/MAP, 2013
Herault, France	23.3	221	248		7.76		UNEP/MAP, 2013
Krka, Croatia	1.81	201	215	90.3	5.46		UNEP/MAP, 2013
Neretva, Croatia	24.3	623	643	241	5.3		UNEP/MAP, 2013
Gediz, Turkey	190	96.4	304		36.8		UNEP/MAP, 2013
Seyhan, Turkey	94	556	744		74.4		UNEP/MAP, 2013
Ceyhan, Turkey	94.7	536	650		29.9		UNEP/MAP, 2013
Kebir-Rhumel, Algeria	12	17	31	13	10	111	Ounissi and Bouchareb, 2013
Kebir West, Algeria	85	92	222	112	88	1117	Ounissi and Bouchareb, 2013
Saf-Saf, Algeria	136	132	296	42	58	2694	Ounissi and Bouchareb, 2013
Seybouse, Algeria	300	47.5	359		8.5	403	Ounissi et al., 2014
Mafragh, Algeria	44	53	111		15	543	Ounissi et al., 2014
Evros, Greece	2.40	11.1	13.46	3.57	1.49		Pitta et al., 2014
Mafragh, Algeria	20.8	78	104.2	4.6	10	257.2	This study
Seybouse, Algeria	18.6	33.4	58.6	6.8	6.3	129.4	This study

The dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) have been recognized as important component with in respective N (Berman and bronk, 2003; Pitta et al., 2014; Zhang et al., 2015) and P (Karl and Björkman, 2001: Rinker and Powell, 2006; Pitta et al., 2014) pools, contributing generally to more than 20% to the total dissolved form. These dissolved organic forms may provide a significant fraction of N or P demand during the dinoflagellate bloom (Mortazavi et al., 2000; Rinker and Powell, 2006; Zhang et al., 2015). The DON is seldom considered in routine survey of water quality (Berman and Bronk, 2003), and is particularly weakly documented in Mediterranean rivers and estuaries (UNEP/MAP, 2013; Pitta et al., 2014).

Concentrations and fractions of DON in MR and SR are comparable to most Mediterranean rivers. In the two rivers the DON maximum production occurred during spring (44-68 µmol L^{-1}) and summer (13-32 µmol L^{-1}), coinciding with phytoplankton biomass increase, as reported in Bronk et al. (2007). Because of the indirect DOP measurement, its concentration seems to be overestimated, and average values reached 2-4 µmol L^{-1} in MR and SR, respectively. These values are not much different from, for example, those of the Evros River, Greece (Pitta et al., 2014), Ebro River (Artigas et al., 2012), Delaware estuary (Volk et al., 2012), and Mississippi River (Rinker and Powell, 2006). The DON and DOP yields (5-7 and 3-7 kg km^{-2} yr^{-1}, respectively, for MR and SR) were very low compared to other Mediterranean rivers (Ounissi and Bouchareb, 2013; UNEP/MAP, 2013). The DON fraction formed only 5-7% of the total N flux, but the DOP fraction reached 17-20% of the total P flux.

4. Particulate materials level and delivery

However, increased NH_4 and PO_4 supply during the dry season has induced large organic matter production, which increased by 3-fold for SR water and 2-fold for MR waters compared to the wet season. Moreover, Chl *a* levels was more much elevated than those of the other Mediterranean Rivers (Table 10). This levels displayed high values during the dry period. Similar seasonal levels and patterns of Chl *a* variability have been reported in many Mediterranean river' outlets (among others, Ebro River: Sabater et al., 2008; Pô River: Berto et al., 2010; Guadiana River: Domingues et al., 2011; Moulouya River: Tovar-Sánchez et al., 2016).

If we assume all the BSi amount is due to diatoms growth and non-living frustules, it may represent only 8-10% of Chl *a* biomass, depending on the river. This low BSi fraction (or diatom content) may imply that large non-siliceous phytoplankton taxa dominated the river' waters. However, BSi concentrations from MR and SR are 1.5-fold the mean (28 µmol L^{-1}) of rivers worldwide (Conley, 1997). Both the dominance of non-siliceous phytoplankton communities and the unbalanced dissolved nutrient availability are signs of eutrophication problems of both river' waters prevailing throughout the seasons. This also results in a very elevated amount of particulate organic carbon (POC), which represented, for example, 3 to 6-fold the mean concentration in the rivers discharging in the North Mediterranean Sea (Table 11).

Table 10. Chlorophyll *a* concentrations (µg L^{-1}) in some selected Mediterranean rivers.

Rivers	Chl a (µg L^{-1})	Source
Rhone, France	2.2	Moutin et al., 1998
Pô, Italy	2-2.6	Berto et al., 2010
Ebro, Spain	5.1	Colella et al., 2016
Nile, Egypt	6.1	Colella et al., 2016
Rhone, France	3.2	Colella et al., 2016
Evros, Greece	5.2	Colella et al., 2016
Axios, Greece	7	Colella et al., 2016
Asi, Turkey	0.3	Colella et al., 2016
Moulouya, Morocco	4	Tovar-Sánchez et al., 2016
Moulouya, Morocco	4.4	Tovar-Sánchez et al., 2016
Moulouya, Morocco	2	Tovar-Sánchez et al., 2016
Mafragh, Algeria	11.62	This study
Seybouse, Algeria	20.55	This study

Despite the high nutrient input during the dry period, the rivers flow lowering (even leading to clogging the catchment' outlets of SR and MR) induced a great organic matter stock, which dominated the SPM components (32-45%: 10 mg L^{-1} of POC). This atypical hydrological functioning (Khélifi-Touhami et al., 2006; Ounissi et al., 2014) favoured such endogenous POC production. However, concentration of the particulate organic nitrogen (PON) was still rather low (0.06-0.13 mg L^{-1}) compared to other Mediterranean rivers (Table 11).

Unlike the dissolved inorganic nutrients, fluxes of organic and particulate matter displayed high values, particularly the POC, POP, Chl *a* and BSi derived from MR catchment. The POC yield reached 875 kg km^{-2} yr^{-1} for MR deliveries and formed 5.4% of the SPM amounts. The SR deliveries contributed only a third to the POC. These topsoil losses remain very low compared to the most mediterranean catchements (e.g. Higueras et al., 2014). Similarly, the BSi yield of MR dominated the deliveries into the Annaba Bay, and represented 31% of TSi, but only represented 14% of the POC inputs. Also the PON:POC ratio was very low, indicating the rapid recycling processes of N over C in both catchments. Within total silicon TSi ($Si(OH)_4$ + BSi), BSi contributed with 29.7 and 32% in SR and MR waters, respectively. The contribution of BSi carried by rivers to the world ocean has been recognized (Conley et al., 1997; Garnier et al., 2002), and as potential bioavailable stock (after dissolution) should be considered in silicon budget and cycling (Krom et al., 2004). For example, when compared to Si:N ratio, the TSi:TN ratio increased to 0.9 and 1.70 at SR and MR outlets, respectively, as their respective BSi:PON

ratio reached 4.3-8.4. The BSi form is often neglected in biogeochemical studies (Billen and Garnier, 2007), although it can represent 20% of the dissolved silica (Garnier et al., 2002). The comparison of particulate matter fluxes is being difficult as data on Mediterranean rivers are sparse and sadly lacking.

Table 11. Particulate organic matter levels (mg L^{-1}) in some selected Mediterranean rivers.

Rivers	POC	PON	POP	Source
Rhône, France		0.12	0.05	Ludwig et al., 2009
Pô, Italy	1.64			Cozzi et al., 2011
Hérault, France	8.4	1.7		Higueras et al., 2014
Orb, France	7.8	1.8		Higueras et al., 2014
Aude, France	4.7	1		Higueras et al., 2014
Têt, France	8	1.6		Higueras et al., 2014
Fluvià, Spain	11.4	1.6		Higueras et al., 2014
Ebro, Spain		0.2	0.08	Higueras et al., 2014
Ter, Spain	7.7	1		Higueras et al., 2014
Tordera, Spain	11.9	1.7		Higueras et al., 2014
Pô, Italy		0.37	0.07	Higueras et al., 2014
Rhône, France	3.6	0.5		Higueras et al., 2014
Seybouse, Algeria	6			Aounallah, 2015
Mafragh, Algeria	10.6	0.06	0.21	This study
Seybouse, Algeria	9.95	0.13	0.23	This study

CHAPTER IV
ATMOSPHERIC WET DEPOSITION OF NUTRIENTS

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ATMOSPHERIC WET DEPOSITION OF NUTRIENTS

1. Precipitation data

Precipitation monitoring data from the Annaba meteorological station over the period 1970-2015 show annual totals in the range 409.5-1126.6 mm yr^{-1}, with averages of 654.50 ±151.17 mm yr^{-1} (Fig. 26a) and marked seasonal cycles with dry summers (Fig. 26b) typical of the Mediterranean season.

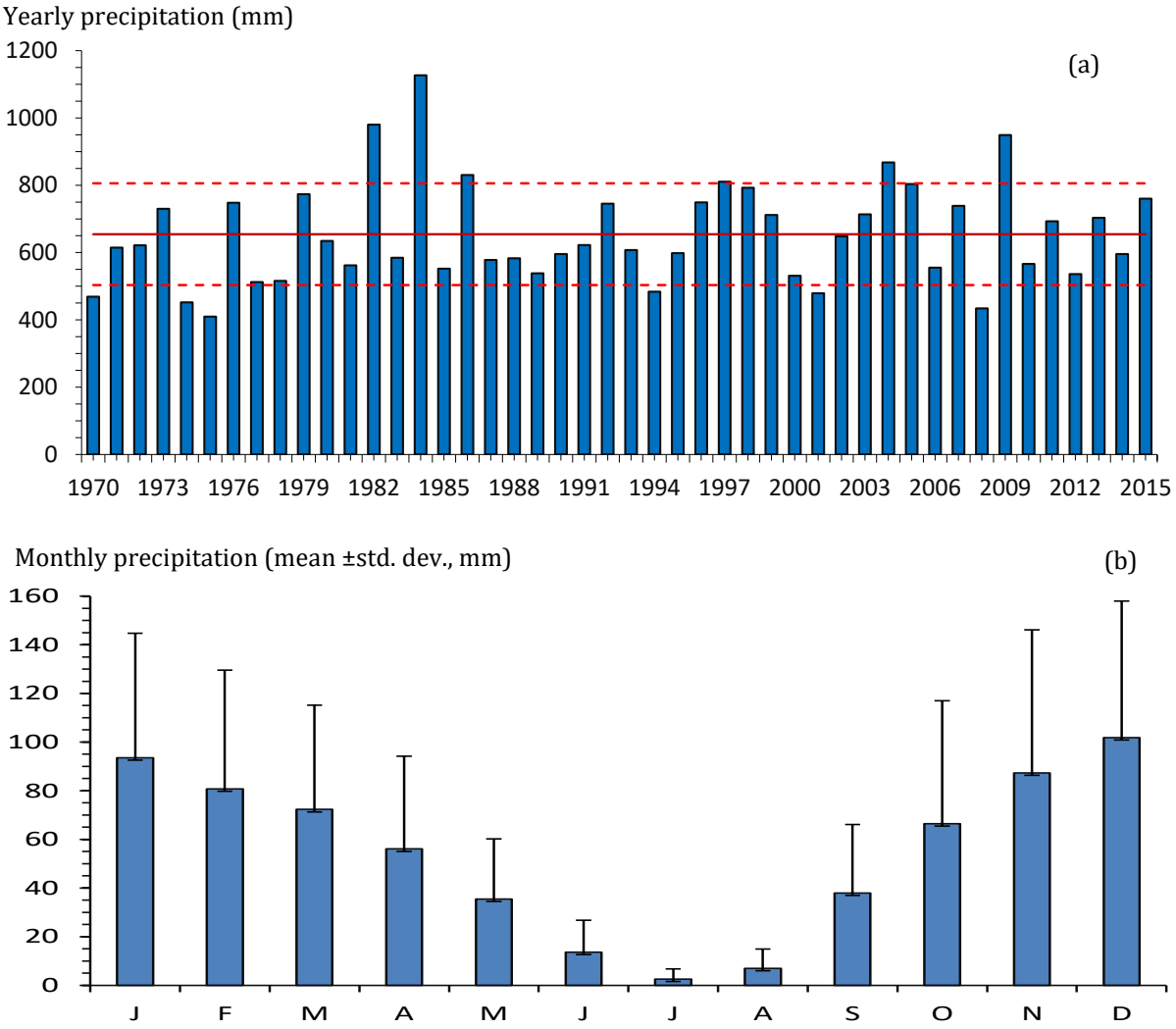

Figure 26. Precipitation at Annaba (lower Seybouse and Mafragh catchments); (a): annual precipitation over the period 1970-2015; the red lines indicate the mean ± the standard deviation; (b): monthly average precipitation and standard deviation at Annaba over the period 1970-2015.

Given a total rainfall of 595.5 mm, 2014 was slightly drier than the mean and included 16, 12, 21, 4, 8, 3, 1, 0, 5, 9, 5, and 16 rainy days in every month, respectively, from January to December (Fig. 27). The seasonal cycle in 2014 somewhat differed from the

typical one because the total precipitation over several months was outside their respective average monthly means $\pm\sigma$.

Two strong precipitation maxima in March and December 2014 compensated for the fact that all other months were significantly drier than usual. As many as 22 rainy days in 2014 had precipitation <1 mm, and 61 experienced more than 2 mm of precipitation, among which 7 days experienced 20 mm or more (46 mm on 7 Dec., 38.2 mm on 7 Nov., 27.4 mm on 4 Oct., 25.1 mm on 5 Mar., 23.1 mm on 28 Jan., 20.1 mm on 5 Oct., and 20.0 mm on 10 Dec.) and nine other days ranged between 10 and 20 mm (Fig. 27). The 16 days with the largest precipitation amounted to more than half of the total annual precipitation (54.5%).

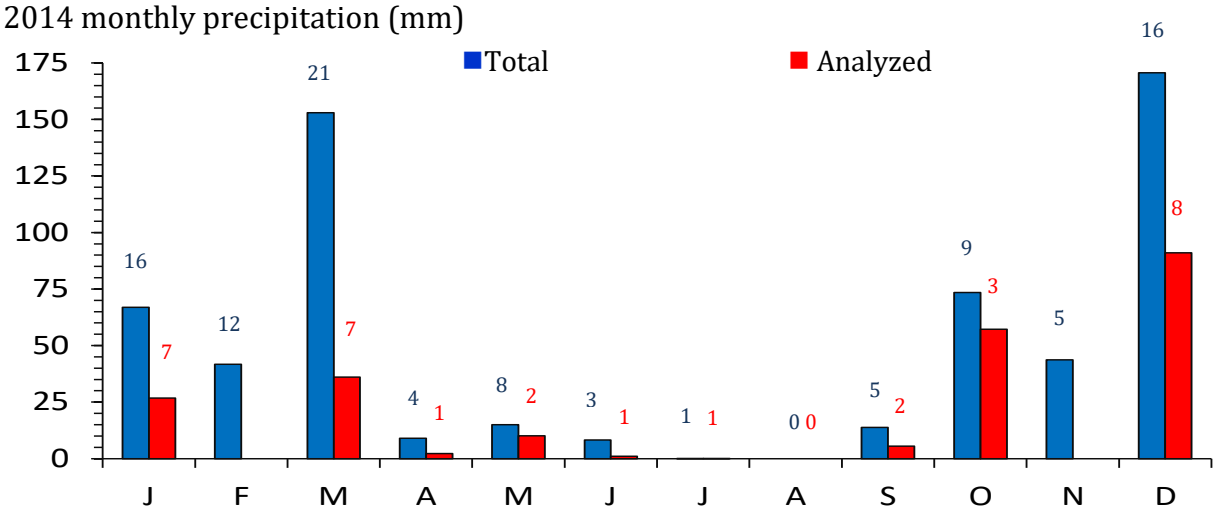

Figure 27. Monthly precipitation (mm) over Annaba region (lower Seybouse and Mafragh catchments) during 2014 with total and analyzed rain events; the numbers indicate the number of days.

2. *Nutrient levels and fluxes in rainwater*

The year 2014 was relatively dry, and the precipitation was less than 600 mm. The rainfall amounts of 36% of the 100 rainy days in 2014 were <2 mm (Fig. 28). The rainiest months were December (170.5 mm) and March (153 mm), which together provided more than half the precipitation yield in that year.

The dissolved nutrient seasonal variations are shown in Figure 28. Overall, the precipitation over Annaba Bay was highly charged with SiO_4 and PO_4 (Fig. 28), which respectively amounted to 16.70 and 1.54 µmol L^{-1}.

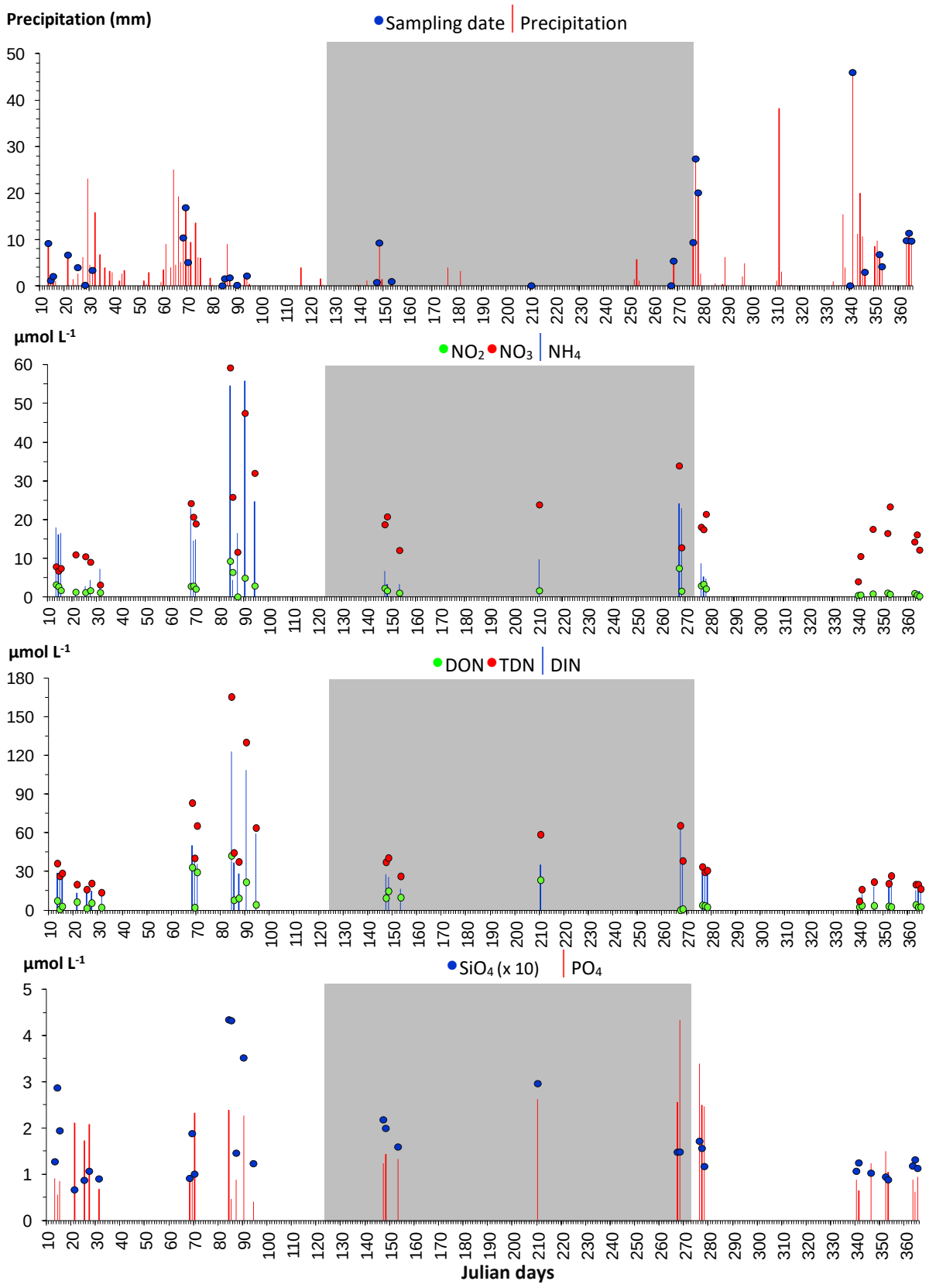

Figure 28. Seasonal variations in precipitation (top) and nutrient levels in the wet atmospheric deposition samples during 2014. The gray area represents the dry season.

However, the concentrations of nitrogen compounds displayed low values; the TDN average value did not exceed 40.5 µmol L^{-1}, of which NO_3, NH_4 and DON represented 45%, 28.4% and 20%, respectively.

The DIN concentration increased by 10% during the dry period, but PO_4 and SiO_4 displayed high levels, increasing by 64% and 21%, respectively, over the values in the wet period (Fig. 28). Apart from PO_4, all nutrients had maximum concentrations during summer, in particular NO_3 (28 µmol L^{-1}), DON (17.3 µmol L^{-1}), SiO_4 (22.9 µmol L^{-1}) and NH_4 (21.9 µmol L^{-1}). In addition, with the exception of NH_4 and NO_2, all the nutrients dropped to their lowest values during winter (Fig. 28). Moreover, low rainfall days were generally heavily charged with dissolved nutrients in comparison to high rainfall days. However, several rainwater samples from spring and autumn had elevated amounts of SiO_4 and PO_4 (Fig. 28).

The average N:P ratio (30) was not much different from that of the riverine waters, but only 37% of the samples were situated within the range 8>N:P<30. The remaining samples with 8<N:P>30 can be considered to be similar to the standard Redfield ratio. The average value of Si:N (0.66) was found to be remarkably comparable to that of the SR waters. Moreover, almost all samples, with the exception of 4, showed low Si:N (<1). This shows the strong dominance of P and Si relative to N in the WAD over the Annaba area (Table 12). Indeed, the WAD over the Annaba area was characterized by a low DIN flux (14.40 mmol m^{-2} yr^{-1}) but high fluxes of Si-SiO_4 (8.10 mmol m^{-2} yr^{-1}) and P-PO_4 (0.88 mmol m^{-2} yr^{-1}) (Table 12).

Table 12. Annual fluxes (mmol m^{-2} yr^{-1}) of dissolved nutrients in rainwater over Annaba region in 2014.

	Wet atmospheric deposition mmol m^{-2} yr^{-1}
NH_4	3.92
NO_2	1.07
NO_3	9.50
DIN	14.40
DON	3.43
TDN	17.83
PO_4	0.88
$Si(OH)_4$	8.10

3. Discussion

Atmospheric deposition is a significant source of nutrients entering the Mediterranean Sea (Koçak et al., 2010; Christodoulaki et al., 2013; Im et al., 2013; Richon et al., 2017), as river discharge and nutrient fluxes have decreased due to dams retention and climate change (Humborg et al., 2000; Ludwig et al., 2009; Lehner et al., 2011). Rainwater in the Annaba region is characterized by high $Si(OH)_4$ and PO_4 concentration in comparison to other Mediterranean sites (Herut et al., 1999; Mace et al., 2003; Markaki et al., 2003; Chen et al., 2007; Koçak et al., 2010; Izquierdo and Avila, 2012; Violaki et al., 2017) (Table 12). $Si(OH)_4$ and PO_4 levels increased during the dry period, when airflow originating from the Algerian desert was predominant. Koçak et al. (2010) found a comparable Saharan dust load effect for the northeast Mediterranean Sea (Table 13).

The WAD of DIN and DON over the Annaba area were oppositely among the lowest in the Mediterranean region (e.g., Mace et al., 2003; Chen et al., 2007; Koçak et al., 2010; Violaki et al., 2010; Izquierdo and Avila, 2012).

Table 13. Wet atmospheric concentration (µmol L^{-1}) of dissolved nutrients in some selected Mediterranean regions.

Station	NH_4	NO_3	DIN	DON	PO_4	$Si(OH)_4$	Sources
Montseny, Spain	20.4	30.2	51				Avila et al., 1998
Tel shikmona, Palestine	25	41	69.04		0.6		Herut et al.,1999
Ashdod, Palestine	35.8	12.94	48.47		0.6		Herut et al., 2000
Erdemli, Turkey	40.3	32.4	73	15			Mace et al., 2003
Heraklion, Greece	21	18	39		0.1		Markaki et al., 2003
Pallanza, Italy	52	40	92				Rogora et al., 2004
Gulf of Aqaba, Palestine	25	39	65	8	0.4		Chen et al., 2007
Erdemli, Turkey	46	44	93		0.7	1.9	Kocak et al., 2010
Finokalia, Crete				23			Violaki et al., 2010
La Castanya, Spain	40.2	33.5	74				Izquierdo et al., 2012
This study	11.5	18.4	32.2	8.3	1.5	16.7	This study

Although the abundance of TDN on the northern Mediterranean side can be related to polluted airflow from Europe (Mace et al., 2003; Koçak et al., 2010; Richon et al., 2017), the low depositions of TDN components may be due to the relatively low human activities (agriculture, transportation and industries) in the Annaba region and to the washout of European air masses before reaching North Africa.

Similar to most Mediterranean coastal sites (Table 14), the DON flux in Annaba rainwater contributed significantly to the TDN pool and represented 20% (Table 14). The main particularity of the Annaba atmosphere is the strong wet depositions of Si-$Si(OH)_4$ and P-PO_4, which are 3-12-fold and 2.5-fold the average Mediterranean values, respectively (Table 14).

Table 14. Specific fluxes (mmol m^{-2} yr^{-1}) of nutrients from wet atmospheric deposition over selected Mediterranean coastal area.

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Site	NH_4	NO_3	DIN	DON	PO_4	$Si(OH)_4$	Source
Cap Ferrat, France			50		0.37		Migon et al., 1989
Corsica					0.43[a]	00-6.7	Tréguer et al., 1995
Northern Israel coast			23.9		0.23		Herut and Krom, 1996
South East Mediterranean			28.5		0.21		Herut and Krom, 1996
Tel shikmona, Israel	13	20	33		0.3		Herut et al., 1999
Ashdod, Israel	19.2	6.9	26		0.2		Herut et al., 1999
Heraklion, Crete			24				Kouvarakis et al., 2001
Finokalia, Crete			17				Kouvarakis et al., 2001
Erdemli, Turkey		16					Markaki et al., 2003
Heraklion, Crete	11	9	20		0.7		Markaki et al., 2003
Erdemli, Turkey	23	22	45		0.34	0.92	Koçak et al., 2010
Erdemli, Turkey [b]	16	13	29		0.18	0.54	Koçak et al., 2010
Erdemli, Turkey [c]	7	9	16		0.16	0.38	Koçak et al., 2010
Cap Spartel, Morocco			28.2		0.7		Markaki et al., 2010
Cap Bear, France			45.9		0.6		Markaki et al., 2010
Ostriconi, France			25.4		0.5		Markaki et al., 2010
Mahdia, Tunisia			18.1		0.4		Markaki et al., 2010
Gozo, Malta			46.1		0.4		Markaki et al., 2010
Finokalia, Greece			39.1		0.2		Markaki et al., 2010
Mytilene, Greece			28.9		0.3		Markaki et al., 2010
Alexandria, Egypt			77.9		0.5		Markaki et al., 2010
Cavo Greco, Cyprus			47.7		0.5		Markaki et al., 2010
Akkuyu, Turkey			30,6		0.4		Markaki et al., 2010
Finokalia, Crete	31.6	45.7	77.3	22.7			Violaki et al., 2010
Zmiinyi Island, Ukraine	13.4	10.2	23.2		0.97		Medinets and Medinets, 2012
La Castanya, NE Spain	26.5	17.3					Izquierdo and Avila, 2012
Cap Ferrat, France			35		0.11		De Fommervault et al., 2015
Erdemli, Turkey	22.6	21.9	44.5		0.33	0.91	Koçak et al., 2015
Sinop, Turkey	0.7	2.2	2.9		0.27		Koçak et al., 2016
Finokalia, Crete					0.6		Violaki et al., 2017
Frioul Island, France				11.9			Djaoudi et al., 2017
Erdemli, Turkey	14.3	11.7	26	10.7			Nehir and Koçak, 2017
Annaba, Algeria	3.9	9.5	14.4	3.4	0.9	9.10	This study

[a] Bergametti et al., 1992
[b] winter
[c] spring and autumn

These high deposition fluxes may be related to eolian Saharan dust exported from North Africa (Moulin et al., 1998; Tréguer and De La Rocha, 2013; Varga et al., 2014; Koçak, 2015; Gkikas et al., 2016; Richon et al., 2017) and partially to local anthropogenic dust injection. In contrast, and because of the low human activities, the DON and DIN fluxes were three times lower than the average values for the Mediterranean region (Table 14).

Obviously, the atmospheric contribution derived from wet deposition sampling in this work is clearly underestimated because the study region is also exposed to atmospheric dry deposition of Saharan dust that we did not sample. From weekly samplings of insoluble atmospheric deposition monitored at Lampedusa Island (35.52°N, 12.63°E, approximately 460 km ESE from Annaba), Vincent et al. (2015) report that dry deposition accounted for 46% of the total dust deposition associated with the 37 most intense deposition events observed from September 2011 to December 2013, which themselves accounted for 84% of the total dust deposition recorded over the period.

CHAPTER V
ATMOSPHERIC DEPOSITION VERSUS RIVERINE NUTRIENT INPUTS

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ATMOSPHERIC DEPOSITION VERSUS RIVERINE NUTRIENT INPUTS

1. Atmospheric deposition versus riverine nutrient inputs

In table 15, we compare the fluxes of the various dissolved and particulate materials from riverine and atmospheric sources. The N:P ratios in the atmospheric inputs (~10) were remarkably comparable to those of the riverine inputs, and the Si:N ratio reached 0.6 under wet atmospheric deposition (WAD). This shows the strong dominance of P and Si relative to N in the WAD over the Annaba area. Indeed, the WAD over the Annaba area was characterized by a low DIN flux (14.40 mmol m^{-2} yr^{-1}) but high fluxes of Si-SiO_4 (8.10 mmol m^{-2} yr^{-1}) and P-PO_4 (0.88 mmol m^{-2} yr^{-1}).

Table 15. Annual fluxes (kg yr^{-1} and mmol yr^{-1}) of dissolved materials from riverine and atmospheric sources estimated for 2014. AA: Annaba area. AB: Annaba Bay, for which the wet atmospheric deposition has been converted to 10^3 kg yr^{-1} by multiplying the flux over AA (mmol m^{-2} yr^{-1}) by its surface area (400 km^2).

	Rivers		wet atmospheric deposition		Ratio
		SR+MR	AB	AA	SR+MR/AB
	10^3 kg yr^{-1}	10^6 mmol yr^{-1}	10^3 kg yr^{-1}	mmol m^{-2} yr^{-1}	
NH_4	187.7	13.4	21.9	3.92	8.50
NO_2	55.9	4.0	5.9	1.07	9.30
NO_3	467	33.4	52.7	9.50	8.86
DIN	711	50.7	80.7	14.40	8.81
DON	51.7	3.64	19.2	3.43	2.70
TDN	762.6	54.5	99.8	17.83	7.60
PO_4	72.8	2.35	10.88	0.88	6.70
$Si(OH)_4$	1663	59.4	90.67	8.10	18.30

The TDN amount was 7.6-fold the WAD (99.8 10^3 kg yr^{-1}) into Annaba Bay (Table 15). The DIN was the major component of TDN for both atmospheric depositions (80.1%) and riverine (89.2%) inputs when compared to the DON fraction (Table 15). Within the DIN form, N-NO_3 was the major component in the WAD (65.4%) and riverine (65.7%) inputs. The N-NH_4 flux was half the N-NO_3 flux in the WAD, contributing only 3920 µmol m^{-2} yr^{-1} (Table 15), it was 8-fold lower than the riverine flux. Compared to the Mafragh inputs, rainwater was an important source of DON (19.2 10^3 kg yr^{-1}) entering Annaba Bay and represented 43% of the sum of the MR and SR inputs. The riverine inputs of P-PO_4 (10.9 10^3 kg yr^{-1}) were approximately 7-fold higher than the atmospheric deposition (Table 15). However, the WAD over the Annaba area was heavily charged with P-PO_4 (878 µmol m^{-2} yr^{-1}). In contrast to the nitrogen and

phosphorus river deliveries, WAD was 18-fold lower than the river input in terms of Si-SiO_4.

2. Discussion

In addition to evaluating the relative importance of the dissolved and particulate matter inputs into Annaba Bay across the MR and SR outlets, this study also assessed the relative contributions of riverine and wet atmospheric inputs of dissolved nutrients into Annaba Bay. The riverine inputs were found to be the main source of dissolved nutrients entering Annaba Bay. They were 8.8-fold, 6.7-fold, 2.7-fold and 18-fold the atmospheric fluxes of DIN, P-PO_4, DON and Si-$Si(OH)_4$, respectively. The superiority of atmospheric deposition over river inputs has been reported in the northeast Mediterranean region (Koçak et al., 2010) for DIN and P-PO_4, but rivers input of S-$Si(OH)_4$ were 10-fold those of rainwater. However, estimates by Martin et al. (1989) showed that DIN river inputs were just comparable to rainwater and that phosphorus loads primarily originated from river runoff. Moreover, the review of Durrieu de Madron et al. (2011) reported that atmospheric deposition can be the main external nutrient supply (Bartoli et al., 2005; Guieu et al., 2010) for the Mediterranean open waters, and more importantly episodes of Saharan dust deposition can enhance the primary production (Ridame and Guieu, 2002; Bonnet et al., 2006; Guieu et al., 2014).

As a consequence of the high dust load from the Algerian desert, the rainwater over the Annaba coastal area is heavily loaded with phosphate and silicate compared to other Mediterranean regions (e.g., Herut et al., 1999; Markaki et al., 2003, 2010; Koçak et al., 2010). In addition, because of the abundance of both phosphorus and silicon in rainwater, the Redfield ratios are not far from those of the rivers but are very different from the ratios in Mediterranean rainwater reported by Herut et al. (1999), Markaki et al. (2003, 2010), Koçak et al. (2010) and Durrieu de Madron et al. (2011).

Table 16 provides the nutrient fluxes from both riverine and atmospheric sources for different world ecosystems, and shows large variability between rivers and atmospheres flux and contribution. For instance, the riverine loads of DIN may vary from 5.8 mmol m^{-2} yr^{-1} in the Yellow Sea to 195 mmol m^{-2} yr^{-1} in the Black sea; 0.27 mmol DIP m^{-2} yr^{-1} in East China Sea to 5 mmol DIP m^{-2} yr^{-1} in the Black sea; 14 mmol DSi m^{-2} yr^{-1} in the Western Mediterranean to 173 mmol DSi m^{-2} yr^{-1} in the Southern yellow Sea.

As shown in table 16, most of these marine systems receive more DIN from atmospheric deposition than river inputs. However, the black Sea, Southern Yellow Sea, East China Sea and North sea showed the dominance of river input over the atmospheric one (Table 16). At the opposite, rivers are the dominant source of DIP and DSi inputs in most Mediterranean and world marine areas, as can be seen in table 16.

As for riverine inputs, there is a strong variability of atmospheric nutrient supplies over the ocean world. In rainwater DIN flux varied between 2.9 mmol m^{-2} yr^{-1} in Sinop to 500 mmol m^{-2} yr^{-1} in the Baltic Sea; 0.07 mmol DIP m^{-2} yr^{-1} in Heraklion to 4 mmol DIP m^{-2} yr^{-1} in West Mediterranean; 0.78 mmol DSi m^{-2} yr^{-1} in East Mediterranean to 9.1 mmol DSi m^{-2} yr^{-1} in Annaba area of the Northestern Mediterranean. This high atmospheric deposition variability of nutrients resulted in differential primary production. Atmospheric deposition of nitrogen can account for 35-60% of new production in the Mediterranean Sea (Christodoulaki et al., 2013), up to 5% in the black Sea (Koçak et al., 2016) and up to 9.2% in the Yellow Sea (Zou et al., 2000). According to Violaki et al. (2017), atmospheric deposition of phosphorus can sustain 14 and 38% of new production in the NW Mediterranean and the Eastern Mediterranean during the oligotrophic period, respectively. However, the phosphorus deposition can enhance the primary production by 5% in the eutrophic black Sea (Koçak et al., 2016) and sustain 38% in the SE Mediterranean (Markaki et al., 2003).

It is clear that rainwater represents a relevant source of fertilizers to marine waters and agricultural land in the Annaba area and can compensate for the loss of nutrients due to dam retention and soil erosion in coastal catchments. Future studies including wet and dry atmospheric and riverine inputs of dissolved and particulate matter will provide a clearer picture on the Mediterranean Sea atmosphere-land interactions.

Table 16. Riverine versus atmospheric inputs (mmol m^{-2} yr^{-1}) of nutrients for different world marine ecosystems. 1mmol N-NH_4, N-NO_3, DIN = 14 mg; 1mmol P-PO_4 =31 mg; 1mmol Si-SiO_4 = 28 mg. For example 33 mmol DIN m^{-2} yr^{-1} =460 mg.

	NH_4	NO_3	DIN	DIP	$Si(OH)_4$	Reference
Western Mediterranean						
Western Mediterranean			33	4.0		Martin et al., 1989
Cap Ferrat, France			52	0.37		Migon et al., 1989
Capo Cavallo, Corsica				0.43		Bergametti et al., 1992
Corsica					0.0-6.7	Tréguer et al., 1995
Annaba, Algeria	3.9	9.5	14.4	0.9	9.1	This study
Cap Ferrat, France			35	0.11		De Fommervault et al., 2015
Riverine			34.3	5.5		UNEP, 1984
Riverine			21	1	15	Ludwig et al., 2009
Eastern Mediterranean						
Wet atmos. Deposition						
Tel Shikmona, Israel	13	20	33	0.3		Herut et al., 1999
Heraklion, Crete	11	9	20	0.07		Markaki et al., 2003
Erdemli, Turkey	23	22	45	0.92	0.92	Koçak et al., 2010
Atmos. Deposition						
Tel Shikmona, Israel	24	40	64	0.81		Herut et al., 1999; 2002
Finokalia, Crete	13	19	32	0.15		Markaki et al., 2003
Erdemli, Turkey	26	44	70	1.14	1.46	Koçak et al., 2010
Eastern Mediterranean					0.78	Krom et al., 2014
Riverine			21	1	14	Ludwig et al., 2009
Mediterranean						
Atmos. Deposition			31.97	0.90		Guerzoni et al., 1999
Riverine			28.75	1.88		Guerzoni et al., 1999
Black Sea						
Wet atmos. deposition						
Western Black Sea	13	10.2	23.2	0.97		Medinets and Medinets, 2012
Sinop, Turkey	0.7	2.2	2.9	0.27		Koçak et al., 2016
Atmos. Deposition						
Western Black Sea	31.9	17.5	49.4	3.13		Medinets and Medinets, 2012
Sinop, Turkey	2.1	4.8	6.9	0.54		Koçak et al., 2016
Varna, Bulgaria	7.8	16.5	24.3	1.66		Koçak et al., 2016
Riverine			195	5	67	Ludwig et al., 2009
Baltic Seas						
Atmos. deposition			500			Voss et al., 2005
Riverine			157			Voss et al., 2005
North Sea						
Atmos. deposition			39			Rendell et al., 1993
Riverine			100			Rendell et al., 1993
Northeast United States						
Atmos. deposition		85.7				Howarth et al., 2002
Riverine		56.4				Howarth et al., 2002
Southern California Bight						
Atmos. deposition [a]	16	25	41			Howard et al., 2014
Riverine [a]	6	32	38			Howard et al., 2014
Yellow Sea and Bohai Sea						
Atmos. deposition			165			Bashkin et al., 2002
Riverine			5.8			Tong et al., 2015
The Southern Yellow Sea						
Atmos. deposition	23.8	28.1	52	0.72	2.6	Song, 2011
Riverine	7.7	48.7	57	0.59	173	Song, 2011
East China Sea						
Atmos. deposition	3.20	14.1	105[b]	0.32	3.42	Song, 2011
Riverine	18.7	24.1	125[c]	0.27	45.7	Song, 2011
Yellow sea and East of China						
Wet atmos. deposition					2.6	Zhang et al., 2005
Sea of Japan						
Atmos. deposition			79			Sugimoto et al., 2017
Kita River			84			Sugimoto et al., 2017
Atmos. deposition			79			Sugimoto et al., 2017
Minami River			56			Sugimoto et al., 2017

Atmos. deposition: wet + dry atmospheric deposition.

[a] mean of California Bight coastal waters (Santa Barbara, Ventura, Santa Monica Bay, San Pedro, North San Diego, San Diego) and their respective river basins input.

[b] Tong et al., 2015.

CONCLUSIONS

CONCLUSIONS

This study assessed for the first time the relative contributions of riverine and wet atmospheric inputs of materials into the Annaba area on the Algerian coast based on extensive sampling and chemical analyses (54 river water samples from the Mafragh and Seybouse Rivers and 32 rainwater samples) in the relatively dry year of 2014, as characterized by an unusually dry period from April to November. The wet atmospheric deposition contributed 5-37% of the riverine inputs, depending on the element, and constituted an important source of dissolved nutrients entering Annaba Bay.

Although the DIN and DON levels in the WAD in the Annaba area were among the lowest in the Mediterranean region, the rainwater in the Annaba region was characterized by high levels of $Si(OH)_4$ and PO_4, which increased during the dry period when high Saharan dust load events occurred with airflows originating over the Algerian desert. This phenomenon resulted in a strong WAD of Si-$Si(OH)_4$ and P-PO_4, which showed 3 to 12-fold and 2.5-fold increases over the average Mediterranean concentrations, respectively.

The decreased riverine discharge during 2014 resulted in low loadings of all dissolved nutrients, whereas the yields of particulate matter (POC, POP, Chl *a* and BSi) displayed high values, especially at the MR catchment's outlet, which could have enriched the receiving coastal waters.

As for the particulate forms of N (NOP) and P (POP), the respective dissolved organic forms (DON and DOP) were found to significantly contribute to the total flux and should thus be considered in N and P budgets and cycling. Those organic forms contributed up to 50% (DOP+POP) and 12% (DON+PON) of their respective total fluxes (TP and TN, respectively). Similarly, at both rivers' outlets, the BSi represented 30-32% of the TSi riverine flux into Annaba Bay and should be better included in routine monitoring programs.

Although the levels of all materials in MR water were always lower than those in SR, the specific fluxes from MR surpassed by several-fold those of SR, which is usually considered to be the most developed catchment. Considering its high specific flow and water discharge, the MR can be assumed to be the most important river in Algeria. Moreover, the MR water had roughly comparable concentrations of dissolved nutrients (except $Si(OH)_4$) to those of rainwater and appeared to function as a nearly pristine ecosystem, with low nutrient levels and more balanced Redfield ratios.

In SR water, the concentration of $Si(OH)_4$ was 3-fold lower than the mean value of the world's rivers, but the PO_4 and NH_4 concentrations remained elevated when compared to the major Mediterranean rivers, in which those nutrient concentrations are decreasing. The SR waters were thus disturbed, as the N:P and Si:N molar ratios were unbalanced in most samples. Those disturbances might explain not only the large phytoplankton biomass but also the lowering of diatom fractions (BSi:Chl *a* ≈0.10) and probably the development of non-siliceous phytoplankton species.

However, it seems that rainwater can be a relevant source of fertilizers for agricultural land and open marine waters in the Annaba area and can partially compensate for the loss of $Si(OH)_4$ due to dam retention and soil erosion in the coastal catchments.

Finally, we must emphasize that the atmospheric contribution derived from wet deposition sampling in this work was clearly underestimated because the study region is also exposed to atmospheric dry deposition of Saharan dust.

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Riverine and wet atmospheric inputs of materials to a North Africa coastal site (Annaba Bay, Algeria)

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Mediterranean Sea

ABSTRACT

This study simultaneously assesses for the first time the relative contributions of riverine and wet atmospheric inputs of materials into the Algerian Annaba Bay on the Mediterranean coast of North Africa. Surface water sampling and water discharge estimates were performed weekly in 2014 at the outlets of the Mafragh River (MR) and Seybouse River (SR). Riverine samples were analyzed for dissolved nutrients and particulate matter (suspended particulate matter: SPM; particulate organic carbon: POC; biogenic silica: BSi; chlorophyll *a*: Chl *a*; particulate organic nitrogen: PON and particulate organic phosphorus (POP). Rainwater samples were jointly collected at a close weather station on a daily basis and analyzed for dissolved nutrients. The rainwater from the Annaba region was characterized by high concentrations of phosphate (PO_4) and silicic acid ($Si(OH)_4$) that are several times the average Mediterranean values, and by strong deposition fluxes. Conversely, the levels of dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON) and associated fluxes were remarkably low. The dissolved nutrient fluxes for the two catchments were low following the lowering of the river flows, but those of particulate matter (POC, Chl *a*, BSi) displayed significant amounts, especially for the MR catchment. BSi and POP represented approximately a third of the total silicon and total phosphorus fluxes, respectively. The levels of dissolved N and P in the MR water were comparable to those in rainwater. MR appeared to be a nearly pristine ecosystem with low nutrient levels and almost balanced N:P and Si:N ratios. SR water had low $Si(OH)_4$ levels but was highly charged with NH_4 and PO_4 and showed unbalanced N:P and Si:N ratios in almost all samples. These conditions have resulted in large phytoplankton biomasses, which may lead to eutrophication. More importantly, the rainwater was identified as a relevant source of fertilizers for marine waters and agricultural land in the Annaba area and can partially balance the loss of $Si(OH)_4$ from rivers to the bay due to dam retention.

1. Introduction

The Mediterranean Sea is one of the most oligotrophic seas in the world, where external inputs of nutrients are especially important to sustaining primary productivity (Margalef, 1985; Béthoux et al., 1998). Mediterranean coastal waters receive various material inputs from riverine, atmospheric and Atlantic water sources (Martin et al., 1989; Béthoux et al., 1998; Ludwig et al., 2010; Durrieu de Madron et al., 2011). But riverine water discharge has declined in the last 50 years (Milliman, 2006; Ludwig et al., 2009) due to increased construction reservoir (Lehner et al., 2011), population growth (CIHEAM, 2009), intensification of agricultural practices, and decreasing trends in precipitation (UNEP/MAP, 2013). The decreases in river discharge are leading to the primary production decrease and oligotrophication of some Mediterranean areas (Umani et al., 2004). In contrast, coastal eutrophication is a consequence of unbalanced riverine nutrient inputs, with excess nitrogen and phosphorus relatively to silica, when compared with the requirements of diatom growth (Conley et al., 1993; Billen and Garnier, 2007).

Indeed, Ludwig et al. (2009) reported that dissolved inorganic nitrogen (DIN) and phosphorus (DIP) inputs from rivers to the Mediterranean Sea may have increased several-fold in recent decades, whereas silicic acid (DSi) levels is expected to decrease due to extensive dam building (Lehner et al., 2011). Dams enhance siliceous sediments retention rates and deplete riverine discharges of dissolved silica, leading to decrease Si:N and Si:P in coastal waters and subsequently

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limitations in diatom growth and marine and estuarine phytoplankton diversity and productivity (Humborg et al., 2000; Ragueneau et al., 2006; Dürr et al., 2011). The molar ratios of N:P:Si have often been used to assess coastal and marine health, and changes in the ratios and in N, P and Si loading and their effects on phytoplankton composition have become topical in coastal oceanographic research (Howarth and Marino, 2006; Billen and Garnier, 2007; Glibert et al., 2013). Aquatic ecosystems can undergo fundamental food web changes as diatom growth is disturbed when the Si:N ratio falls below 1:1 (Turner et al., 1998).

However, studies of river and estuarine modifications at global or regional scales remain lacking (Meybeck, 2003; UNEP/MAP, 2013) and assessing impacts of some river or estuarine syndromes on aquatic resources is considered a first priority. Although a few upwelling sites and frontal regions of limited extent can provide significant nutrient supply to surface Mediterranean waters (Siokou-Frangou et al., 2010), most of the nutrients entering the Mediterranean Sea derive from atmospheric wet and dry depositions and riverine runoff (Martin et al., 1989; Krom et al., 2010; Koçak, 2015). Because riverine nutrients are removed by biological activity in estuarine and adjacent coastal waters, atmospheric inputs are probably the main source of nitrogen to open sea surface waters, even in the northern zones of the Mediterranean (Guerzoni and Molinaroli, 2005; Koçak et al., 2010; Pasqueron de Frommervault et al., 2015). But in the southwestern Mediterranean Sea, atmospheric inputs of nutrients are becoming the main external source due to declining river discharge in recent decades following reservoir construction and changes in irrigation practices (Guerzoni et al., 1999; Guerzoni and Molinaroli, 2005).

Atmospheric inputs of nitrogen have been reported to be equal to the riverine inputs over the entire Mediterranean Sea (Martin et al., 1989; Loÿe-Pilot et al., 1990) and to be dominant in the southern zones (Bashkin et al., 1997). Im et al. (2013) observed that atmospheric deposition provides significant amounts of nutrients to oligotrophic marine ecosystems such as the Mediterranean Sea. Atmospheric deposition of nitrogen may account for up to 35–60% of new production (Christodoulaki et al., 2013), and atmospheric deposition of nitrogen and phosphorus would account for approximately 9% and 38% of total primary production in the Western and Eastern Mediterranean, respectively (Pacciaroni and Crispi, 2007). According to Koçak et al. (2010), the atmospheric deposition of inorganic nitrogen and phosphorus largely dominate the riverine inputs into eastern Mediterranean oligotrophic waters. A number of studies along Mediterranean coasts suggest that atmospheric deposition is expected to strongly influences the biogeochemistry and trophic status of the Mediterranean Sea (Ridame and Guieu, 2002; Herut et al., 2005; Markaki et al., 2010; Violaki et al., 2010; Christodoulaki et al., 2013; Koçak, 2015). For the Mediterranean, wet atmospheric deposition (through rain washout) of N and P is the main source (Guerzoni et al., 1992; Markaki et al., 2003) than dry deposition (direct sinking or sedimentation during periods without rain). The majority of wet deposition occurs during a few intense, episodic and spatially patchy rainfall events (Guerzoni et al., 1999). In addition, the Mediterranean Sea, particularly its southwestern side, is subject to the largest and most persistent aerosol loads, which are primarily located in North Africa (Morales-Baquero et al., 2013; Varga et al., 2014; Vincent et al., 2016).

Assessments of nutrient inputs from both atmospheric and riverine sources into Mediterranean waters are still rare especially in southwestern Mediterranean regions. To our knowledge, the only available simultaneous measurements of riverine and atmospheric inputs of dissolved inorganic nutrient are available in an overview of the Western Mediterranean by Martin et al. (1989) and in the work of Koçak et al. (2010) in the North Levantine Sea (Turkey). Despite the importance of those reference works, the dissolved and particulate forms of N, P and Si have not been considered together in river water, nor dissolved organic nitrogen (DON) in rainwater even thought. According to Markaki et al. (2003), both DON and DOP are important contributors to N and P deposition and account for almost 30% of the total dissolved atmospheric nitrogen and phosphorus load in rainwater. The contribution of DON in stimulating new production in the eastern Mediterranean was estimated to reach 20–30% (Violaki et al., 2010), and DON accounted 23% of total dissolved nitrogen.

Few studies have monitored Si deposition (e.g., Markaki et al., 2010) despite its important role as a plant nutrient and carbon dioxide regulator (Sommer et al., 2006). In addition, as both organic (dissolved and particulate) and inorganic forms of nitrogen are rapidly available to sustain marine phytoplankton (Wiegner and Seitzinger, 2001), they should consequently be considered together when assessing imbalances of riverine nutrient inputs (Billen and Garnier, 2007). Similarly, within phosphorus compounds, particulate inorganic phosphorus represents a significant fraction, a large part of which is desorbed and remobilized in estuarine and marine environments (Conley et al., 1995). Moreover, a significant flux of biogenic particulate silica (derived either from endogenous diatoms or phytoliths eroded from catchment top soils) is also delivered by rivers (Garnier et al., 2002; Sferratore et al., 2006), but that form is seldom measured in monitoring programs. More importantly, silica data are missing from most monitoring programs of Mediterranean rivers (UNEP/MAP, 2013), particularly Algerian coastal rivers (Ounissi and Bouchareb, 2013; Ounissi et al., 2014). It is clear that both organic and inorganic forms of nutrients should be considered in either riverine or atmospheric inputs to obtain a more representative picture of Mediterranean marine ecosystem productivity and biogeochemical cycles.

Information on riverine and atmospheric inputs of materials is still scarce in the Mediterranean basin (Ludwig et al., 2010; Markaki et al., 2010; Violaki et al., 2010; UNEP/MAP, 2013) particularly for Algerian coastal catchments (Ounissi et al., 2014). The Annaba coastal region (northwestern Algeria, Fig. 1) is subject to atmospheric deposition under the main influences of European airflows (October-March) and African air masses with high dust loads (April-September). The region also receives inputs from two important Algerian rivers, namely the Mafragh River (MR) and the Seybouse River (SR). This region is among the wettest areas in Algeria (Laborde et al., 2010). Although the wet atmospheric deposition (WAD) of dissolved nutrients has been recognized as significant in the Mediterranean Sea, data on nutrient wet deposition on Algerian coasts are almost nonexistent. In addition, little is known about nutrient and material transport from Algerian coastal catchments (Ounissi and Bouchareb, 2013; Ounissi et al., 2014). The major efforts have focused on the groundwater quality of the SR and MR catchments, but the surface waters in those areas have only been explored for dissolved nutrients (Ounissi and Bouchareb, 2013; Ounissi et al., 2014, 2016). Due to the specific objectives of those previous studies, particulate matter was not considered, although it is a key component in river and estuarine systems.

The present work is based on an extensive riverine and rainwater data collection during 2014 in the Annaba coastal area of the southwestern Mediterranean. We present the distribution and fluxes of dissolved and particulate material into the Annaba Bay from the Mafragh and Seybouse Rivers together with the WAD of dissolved nutrients. To our knowledge, this is the first assessment of the wet deposition of dissolved nutrients and of particulate biogenic silica, particulate organic carbon, suspended particulate matter and chlorophyll *a* in southwestern Mediterranean waters, including Algerian coastal waters. Our main objectives were to (1) assess the relative contributions of riverine and wet atmospheric inputs of dissolved nutrients (N, P, Si) into Annaba Bay, (2) determine the relative importance of the dissolved and particulate matter transferred into the bay through the two rivers' outlets and (3) assess differences in the material deliveries of the two rivers, which are differently affected by human activities.

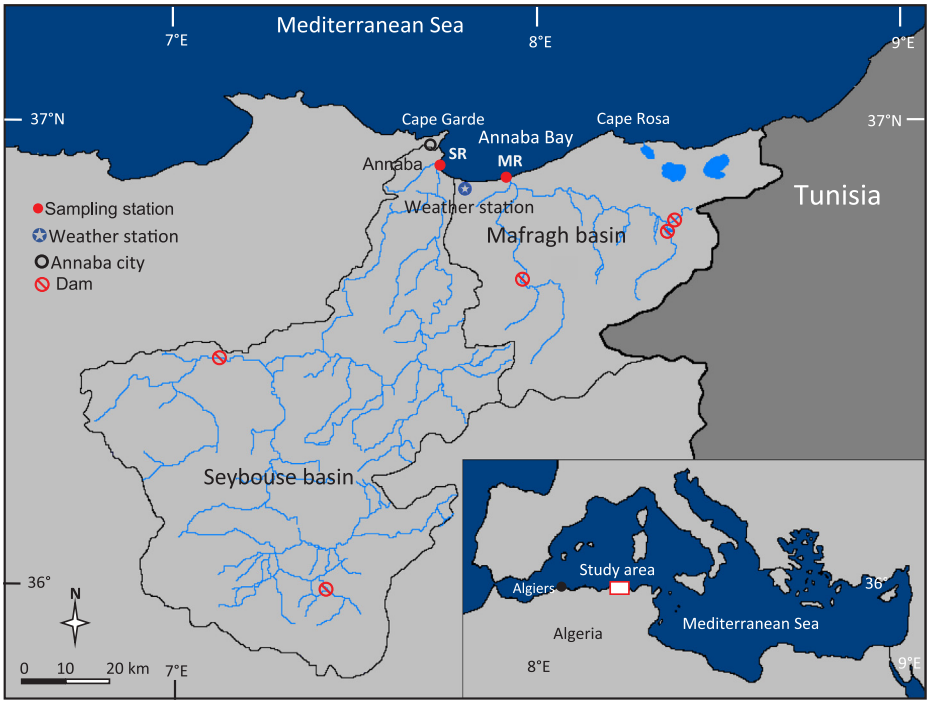

Fig. 1. Map of the Seybouse River (SR) and Mafragh River (MR) catchments and their adjacent coast (Annaba Bay), showing the location of the sampling sites (river outlets and the weather station).

2. Materials and methods

2.1. Sampling sites

Annaba Bay is located at approximately 37°N, 8°E on the north-eastern coast of Algeria (Fig. 1) and between Cape Rosa and Cape Garde. It has a surface area of 400 km^2 and a maximum depth of 70 m. The bay receives continental inputs from the Mafragh River (MR) and Seybouse River (SR) (Fig. 1) and from direct industrial and household wastewater (Ounissi et al., 2008) of over 2 million people. The lower parts of SR and MR are affected by tidal intrusion during the dry season and function as highly stratified estuaries (Khélifi-Touhami et al., 2006; Ounissi et al., 2014). The salt wedges in SR and MR extend as far as 8 and 15 km, respectively (Khélifi-Touhami et al., 2006; Ounissi et al., 2014). With a length of 165 km, a catchment area of 6500 km^2 and a population of approximately 1.5 million inhabitants, SR is among the largest and most developed river systems in Algeria. Intensive agriculture is expanding (3–4% of the total catchment area; UNEP/MAP, 2013) in the middle and lower SR catchments, which is maintained by water retention in reservoirs (400 million m^3). That amount is equivalent to a third to half of the annual precipitation. The flow rate of SR has been reduced to about 14 $m^3 s^{-1}$ (UNEP/MAP, 2013) due to dam retention.

The MR catchment (3200 km^2) is lightly populated (90 inhab. km^{-2}), but intensive agricultural practices are invading most of the middle and lower catchments. Agriculture has been recently described as the main source of nitrogen and phosphorus emissions in this area, which mainly originate from irrigated land (4–5% of the total catchment; UNEP/MAP, 2013) and cattle rearing, in addition to significant road traffic mainly to and from Tunisia. The catchment is largely forested in the upper part but includes large marshlands and floodplains (130 km^2) in the lower part (Fig. 1). By dry season and under low river flows, the MR connection to the sea may be closed for several months. The MR flow rate is highly variable (0–2000 $m^3 s^{-1}$) with the annual mean flow rate of 24 $m^3 s^{-1}$ (UNEP/MAP, 2013).

Sampling sites are situated at the outlets of MR and SR, which are separated by approximately 15 km (Fig. 1). Based on satellite data (Mehta and Yang, 2008), precipitation over the Annaba region varies between 1.25 and 2.25 mm day^{-1} from October to April, with maxima in winter (November-January), similar to most of the southwestern Mediterranean region (Lionello et al., 2012). The rest of the year is dry, despite sporadic storms that occur during the transitional periods (August-September and April-May). The region is mostly under the influence of two contrasting air masses: cold and humid airflow originating from Europe (October-March) and the warm and dry airflow originating from the African desert (April-September). The region is directly affected by high dust loads (Moulin et al., 1998; Varga et al., 2014) and dust deposition (Morales-Baquero et al., 2013; Vincent et al., 2016) from the contiguous Algerian desert during the dry period.

2.2. Analytical methods

2.2.1. Riverine water

2.2.1.1. Water sampling and collection of hydrological data. The surface waters were sampled weekly in 2014, and water discharge and salinity were simultaneously measured. To assess the rivers' water discharges ($m^3 s^{-1}$), the flow velocities at the rivers' outlets were measured using a CM-2 current meter (Toho Dentan Co., Ltd., Tokyo) at the rivers' outlets and calculated by multiplying the water velocities by the total surface areas (m^2) of the rivers' wet sections. Measurements of water velocity were taken at several points along the rivers' sections, which allowed computations of the average current velocities. Water salinity (Practical Salinity Scale: PSS) was measured in situ using a WTW Cond 1970i multi-parameter probe (http://www.wtw.com). Surface water samples were collected from the centers of the river flows for nutrient and particulate organic matter analyses and were immediately pre-filtered after sampling using a sieve filter (200–µm porosity), except for measurements of suspended particulate matter (SPM).

2.2.1.2. Biogeochemical analyses. In the laboratory, the water samples collected for dissolved nutrient analyses were filtered through Whatman GF/C 0.5–µm glass filters. The dissolved nutrients were analyzed on the same or following day. For silicic acid ($Si(OH)_4$) and particulate biogenic silica (BSi) determination, a fraction of each

sample was filtered through polycarbonate filters. Particulate matter was stored at -20 °C for one day and analyzed. The dissolved inorganic nitrogen DIN (ammonia: NH_4; nitrate: NO_3; nitrite: NO_2), dissolved organic nitrogen (DON), phosphate (PO_4) and $Si(OH)_4$ were determined using the standard colorimetric methods described in Parsons et al. (1989). Total dissolved phosphorus (TDP) and polyphosphate (P_2O_5) were measured using the standard method of Rodier (1996). Dissolved organic phosphorus (DOP) was obtained by subtracting the dissolved inorganic phosphorus (DIP = PO_4 + P_2O_5) from TDP.

SPM was measured using two 250–500 ml water subsamples (depending on the sample turbidity) following the method described in Parsons et al. (1989).

Chlorophyll *a* (Chl *a*) was measured according to the method of Lorenzen (1967). As the rivers' outlets are usually highly productive, a water sample of only 250–500 ml was filtered through a Whatman 47–mm GF/C glass filter, and chlorophyll was extracted in a refrigerator for 1 h in pure methanol. Particulate organic carbon (POC) was determined using the titrimetric method of Le Corre (Aminot and Chaussepied, 1983). The volume filtered and the filters were the same as those used for SPM. Biogenic particulate silica (BSi) was determined using to the method of Ragueneau and Tréguer (1994). The particulate biogenic silica retained on the polycarbonate filters was digested to extract the corresponding $Si(OH)_4$, which was analyzed using the standard colorimetric method described in Parsons et al. (1989).

Particulate organic nitrogen (PON) and particulate organic phosphorus (POP) were measured using the method of Raimbault et al. (1999), which consists of oxidizing organic N and P by the action of a persulfate reagent at 120 °C in alkaline buffer conditions to obtain the equivalent mineral forms (NO_3 and PO_4 respectively). NO_3 and PO_4 were determined using the method described in Parsons et al. (1989).

All dissolved nutrients and particulate matter forms were analyzed on duplicate samples (or subsamples). Total phosphorus (TP) is the sum of dissolved and particulate phosphorus forms, total nitrogen (TN) is the sum of dissolved and particulate nitrogen forms, and total silica (TSi = BSi + $Si(OH)_4$) is the sum of dissolved silica ($Si(OH)_4$) and particulate biogenic silica (BSi); the fraction of lithogenic silica is here neglected. The uncertainties are as follows: PO_4: ± 3.4%; NH_4: ± 3.3%; NO_3: ± 2.6%; NO_2: ± 3.7%; $Si(OH)_4$: ± 1.2%; DON: ± 5.5%; P_2O_5: ± 5.2%; TDP: ± 2.7%; POC: ± 5.5%; POP: ± 5%; PON: ± 5%; Chl *a*: ± 5.2%; and BSi: ± 2.4%.

2.2.1.3. Estimation of material fluxes. The annual fluxes of dissolved nutrients and particulate matter were estimated using the method of average instantaneous loads (Preston et al., 1989):

$$F = K \sum_{i=1}^{n} \left(\frac{CiQi}{n} \right),$$

where F is the annual flux (in tons per year or t yr^{-1}), Ci is the concentration of the substance of interest (μmol L^{-1} for dissolved nutrients converted to kg m^{-3} or mg L^{-1} for particulate matter), Qi is the concomitant instantaneous flow (m^3 s^{-1} converted to m^3 $^{-1}$), n is the number of days for which level and flow data are available, and K is a conversion factor used to consider the full year period (365 days) and unit of estimation. This assumes that the average flux derived from measurements can be extrapolated to the whole year. To facilitate comparisons between the two catchments, the fluxes (kg yr^{-1}) were also normalized by the respective catchment area and expressed in kg km^{-2} yr^{-1}.

2.2.2. Rainwater

2.2.2.1. Rainwater collection and precipitation data. Rainwater samples were collected using a rainfall collector (200–cm^2 collecting area; 2–L collecting polyethylene bottle) placed in a cleared and fenced area at the Annaba weather station (36°49′19″N, 7°48′11″E), which is located 3 km from the Annaba Bay coastline, between the two river mouths (Fig. 1) at 5 m above the mean sea level. The sampling site is situated in a rural area but is not very isolated from the main sources of pollution in the region; it is 10 km from Annaba city and its surrounding villages (nearly 1 million inhabitants), 5 km from a large fertilizer factory (Fertial Company) and 10 km from the Arcelor Mittal steel complex of El Hadjar. Those potential sources of pollution may contaminate the local atmosphere.

A total of 100 rainfall days were recorded in 2014 at the Annaba weather station, of which rainfall was analyzed on 32 days. The samples were transferred into polyethylene bottles, transported to the laboratory and analyzed on the same or the following day.

2.2.2.2. Nutrient analyses and fluxes estimation. Like for river water, the rainwater samples were treated and analyzed for different analytical determinations (NH_4, NO_3, NO_2, DON, PO_4, and $Si(OH)_4$). When the quantity of rainfall collected was insufficient for all the chemical analyses, it was diluted with distilled water to obtain the required volumes.

The wet atmospheric deposition fluxes (*Fw*) were computed following Herut et al. (1999). The volume weighted average concentration (*Cw*) in rainwater of the nutrient of interest was first computed from

$$Cw = \frac{\sum_{i=1}^{n} Ciqi}{\sum_{i=1}^{n} qi}$$

where *Ci* is the nutrient concentration, and *qi* is the rainfall amount for a given precipitation event. The wet atmospheric deposition fluxes (*Fw*) of nutrients were then computed by multiplying the volume weighted average concentration of the nutrient of interest by the annual rainfall amount (P_{annual}), assuming that the average flux derived from the set of samples analyzed was representative of the entire year:

$$Fw = Cw\ P_{annual}.$$

The 32 analyzed samples represented a total of 229.7 mm (38.6%) out of the annual total of 595.5 mm. They included 7 daily samples in January, 7 in March, 1 in April, 2 in May, 1 in June, 1 in July, 2 in September, 3 in October, and 8 in December, in agreement with the seasonal cycle of precipitation.

2.3. Statistical analyses

One-way analysis of variance (ANOVA) was performed to compare the difference between weekly samplings of material in the MR and SR outlets with a significance threshold at P = 0.001. When the one-way ANOVA revealed significant differences between weekly samples, a Tukey's honest significant difference (HSD) test was also applied to identify the sources of variation. The data were statistically analyzed using SPSS statistics software version 17.0. The relationships between the 19 biogeochemical parameters measured in 54 samples at each site (SR and MR) were also assessed via the correlation coefficient r computed using the same software. For the 54 correlated pairs, the significance threshold values at $p = 0.001$ and 0.01 are $|r| > 0.44$, $|r| > 0.35$, respectively (Scherrer, 1984).

3. Results

3.1. Precipitation

Monitoring of rainfall data from the Annaba weather station in the period 1970–2015 revealed annual totals ranging from 409.5 to 1126.6 mm yr^{-1}, with an average of 654.50 ± 151.17 mm yr^{-1} and marked seasonal cycles with dry summers (Fig. 2) that are typical of the Mediterranean region.

With total rainfall of 595.5 mm, 2014 was slightly drier than the mean (Fig. 2a) and included 100 rainy days (Fig. 2c). The seasonal cycle in 2014 differed somewhat from the typical one because the total

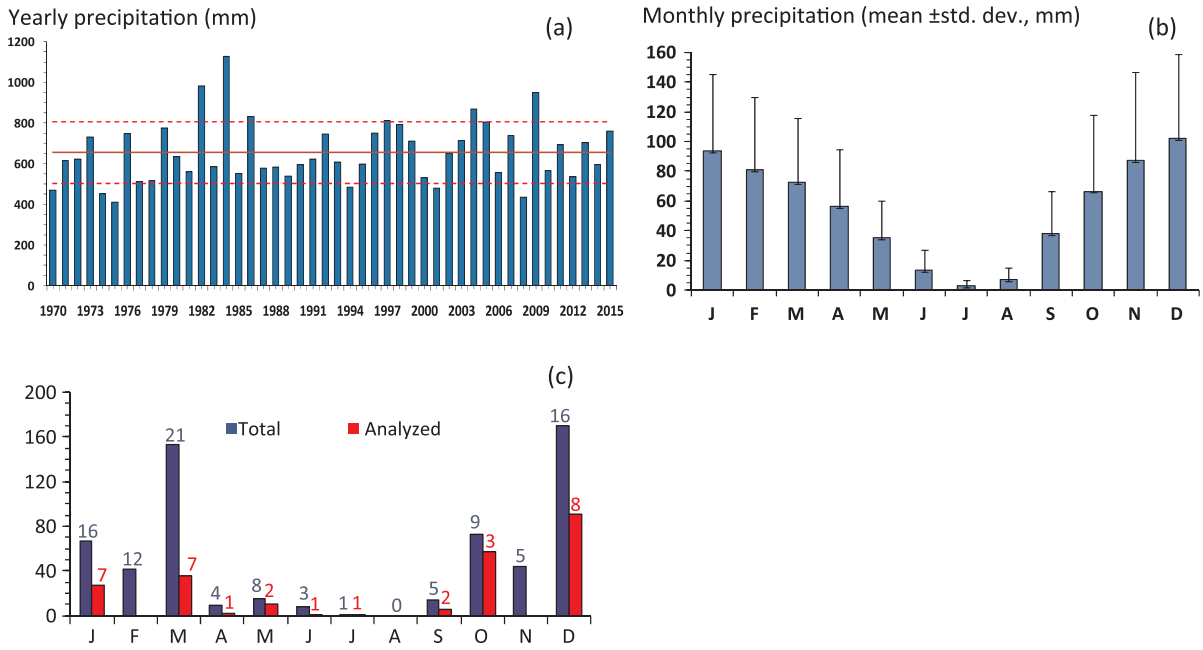

Fig. 2. Precipitation at Annaba (lower Seybouse and Mafragh catchments); (a): annual precipitation over the period 1970–2015; the red lines indicate the mean ± the standard deviation; (b): monthly average precipitation and standard deviation at Annaba over the same period; (c): monthly precipitation in 2014 with total and analyzed rain events; the numbers indicate the number of days with rain in both cases. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

precipitation over several months was outside their respective average monthly means ± σ. Two rainfall maxima in March and December 2014 compensated all drier than usual other months. As many as 22 rainy days in 2014 had precipitation < 1 mm, and 61 had more than 2 mm, among which 7 days had 20 mm or more (46 mm on 7 Dec., 38.2 mm on 7 Nov., 27.4 mm on 4 Oct., 25.1 mm on 5 Mar., 23.1 mm on 28 Jan., 20.1 mm on 5 Oct., and 20.0 mm on 10 Dec.), and on nine other days precipitation ranged between 10 and 20 mm. The 16 days with the highest precipitation accounted for (54.5%) the total annual precipitation.

3.2. Variations in the concentrations of dissolved and particulate material at the rivers' outlets

The freshwater discharges varied greatly throughout the seasons and averaged 15.40 and 11.70 $m^3 s^{-1}$ at the MR and SR outlets, respectively (Fig. 3, top left). The maximum water discharges occurred during November-April, and very low flows (< 1 $m^3 s^{-1}$ on average) occurred during the rest of the year. During the wet period (October-April), the water salinity varied in a small range (0.1–1.4 PSS) for both rivers. The water salinity increased significantly in MR waters (10–33 PSS) during the dry and closing periods (May-September) but remained on the order of 1–2 PSS for SR waters (Fig. 3, top right). MR had been closed from the sea for more than 6 months, from 12 June to 21 December 2014, and SR was nearly disconnected during three weeks in August. As a result of the dry months, the two estuaries only delivered 0.84×10^9 m^3 of water into Annaba Bay over most of 2014.

The mean SPM level was 55 mg L^{-1} at the SR outlet and 61 mg L^{-1} at the MR outlet, with maxima in February for MR (190 mg L^{-1}) and March for SR (465 mg L^{-1}), which coincided with high river flows. There were significant and large correlations between the SPM levels and the water flows ($r = 0.70$ and $r = 0.69$, for MR and SR, respectively: $p < 0.001$). The lower parts of the two estuaries were affected by marine intrusions during low river flows: < 2 $m^3 s^{-1}$ for SR and during the closing period (0 $m^3 s^{-1}$) for MR.

As shown in Fig. 3, at both rivers' outlets, all the nutrient forms varied greatly throughout the year, with usually high values of dissolved nutrients during the wet period, whereas particulate matter (Chl *a*, BSi, PON, POP, and POC) and dissolved organic nutrients (DON, DOP) increased during the dry period (Fig. 3). This large variability was also shown by the one-way ANOVA (Table 1), with significant differences between sampling dates for both dissolved (except NO_2) and particulate matter in a given river. The Tukey HSD post hoc test showed that samples collected during the dry period differed significantly from those collected during the wet period.

All the dissolved nutrients concentrations were always higher in SR than in MR (Fig. 3). However, within the particulate organic matter pool, only the Chl *a* and PON concentrations were more abundant in the SR waters, and the other particulate forms did not differ in the two rivers' outlets.

The mean concentration of total nitrogen (TN) was 47 µmol L^{-1} at the MR outlet but increased to 98 µmol L^{-1} at the SR outlet. Most of the TN was in the form of TDN. The NO_3 fraction represented one half and one third of the TDN in the MR and SR waters, respectively. The oxidized nitrogen form was equal to that of the reduced form (NH_4) in SR waters but was 2-fold higher in MR waters.

The DON was nearly two times more abundant than PON at the MR outlet and 1.5-fold higher at the SR outlet. These two organic nitrogen forms exhibited the same variations and were highly and significantly correlated ($r = 0.82$ at MR, and $r = 0.57$ at SR; $p < 0.001$). The DON concentrations followed a clear seasonal cycle in both rivers, with high values during the dry period that reached 20.70 and 11.90 µmol L^{-1} in SR and MR, respectively. The values during the wet period were half those during the dry period in the two rivers' outlets (Fig. 3).

The DIN concentrations increased during the high river flow (wet period), reaching 43.7 µmol L^{-1}, but dropped to 18.5 µmol L^{-1} in the MR waters during the dry period. Unlike that for MR waters, large amounts of NH_4 were supplied during summer in SR waters (Fig. 3). The NH_4 levels were, in fact, negatively correlated with SR flow ($r = -0.30$, $p < 0.05$). Jointly with the increase in NH_4 level in the dry season (56 µmol L^{-1} in SR), the NO_3 level decreased 3-fold and 5.5-fold in SR and MR waters, respectively. The oxidized nitrogen was largely supplied during wintertime and increased with river flow in both SR ($r = 0.35$, $p < 0.01$) and MR ($r = 0.44$, $p < 0.001$) waters.

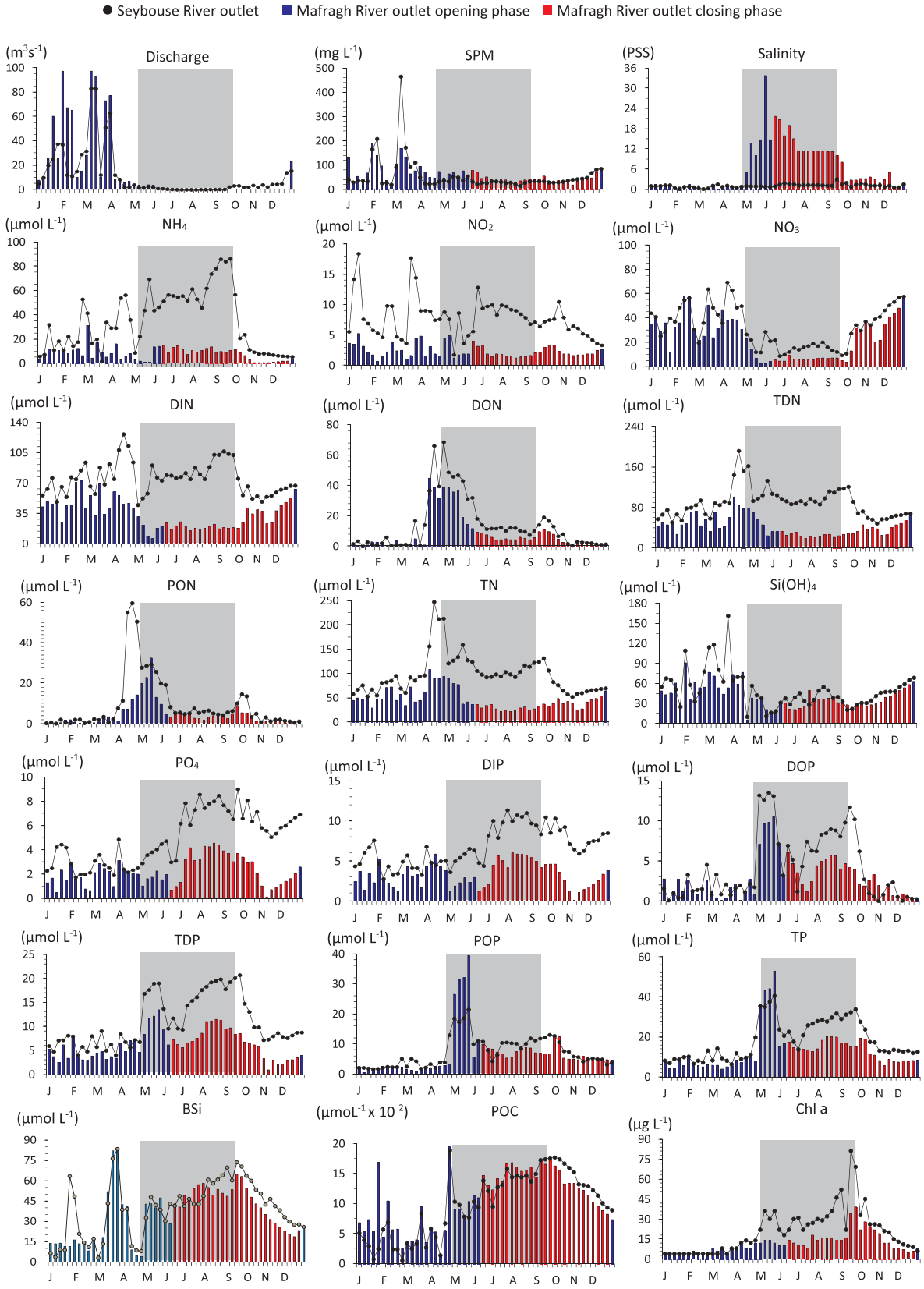

Fig. 3. Seasonal variations in hydrological and biogeochemical parameters at the SR and MR outlets, during January-December 2014. The gray area represents the dry season. The low discharges at the beginning of the wet season (autumn) were due to dam retention. Mafragh River outlet closing phase: the river outlet was closed from its marine tidal connection from 12 June-21 December 2014; Mafragh River outlet opening phase: the river outlet was opened to sea from 01 January-11 June and from 22 to 30 December 2014.

Table 1
One-way ANOVA results (F: Fisher test) showing variation factors between water flow and material concentrations in MR and SR from $n = 54$ weekly samples in 2014; (ns: not significant; highly significant: $p < 0.001^{***}$).

	MR	SR
	F	F
Flow	5.16^{***}	5.90^{***}
SPM	3.14^{***}	3.12^{***}
Sal	29.45^{***}	0.83^{ns}
NH_4	4.43^{***}	13.63^{***}
NO_2	1.69^{ns}	1.34^{ns}
NO_3	14.05^{***}	13.06^{***}
DIN	10.01^{***}	8.33^{***}
DON	14.76^{***}	17.89^{***}
TDN	11.12^{***}	13.48^{***}
PON	16.76^{***}	9.22^{***}
TN	11.76^{***}	13.68^{***}
$Si(OH)_4$	4.40^{***}	6.67^{***}
PO_4	10.73^{***}	35.40^{***}
DIP	8.31^{***}	29.95^{***}
DOP	32.41^{***}	36.39^{***}
TDP	23.80^{***}	46.36^{***}
POP	69.64^{***}	25.95^{***}
TP	63.71^{***}	44.57^{***}
BSi	7.80^{***}	4.58^{***}
Chl *a*	6.64^{***}	16.53^{***}
POC	7.80^{***}	15.80^{***}

The two rivers showed high concentrations of total phosphorus (TP) throughout the seasons, in particular during the dry period (Fig. 3), when the dissolved organic (DOP) and particulate (POP) forms were supplied by the release and development of phytoplankton organisms. Those organic forms of phosphorus were highly and significantly correlated with chlorophyll *a* levels. The correlation coefficients of DOP-Chl *a* were $r = 0.82$ ($p < 0.001$) and 0.34 ($p < 0.01$) for SR and MR, respectively, and the POP-Chl *a* correlation was 0.68 ($p < 0.001$) for SR and only 0.26 ($p < 0.01$) for MR. The TP concentrations were slightly higher in SR (18.4 μmol L^{-1} on average) than in MR waters (13.2 μmol L^{-1}) but had the same seasonal cycle. Within TP, the particulate form was dominant at 53% and 40% at the MR and SR outlets, respectively, and the dissolved organic form also constituted an important fraction (22%) at the two sites. Because DOP may have mainly originated from the degradation of POP, there were large correlations between the two forms in both rivers ($r = 0.80$, $p = 0.001$). Dissolved inorganic phosphorus (DIP) accounted for approximately a third to a fourth of the TP amounts and varied similarly over the seasons. The concentrations of phosphate (PO_4) were, however, higher in SR waters (4.90 μmol L^{-1}) than in MR waters (2.20 μmol L^{-1}) and increased during the dry season by approximately 36% over that in the wet season. At the SR outlet, although the DIN:PO_4 ratio (herein referred to as N:P) average value (19.50) did not deviate much from the standard Redfield ratio (78% of the samples had $8 < N:P > 30$) but deviated greatly from the equilibrium situation (Fig. 4). In MR waters, however, half of the samples had $8 < N:P > 30$, and 25 samples presented comparable values to the Redfield standard ratio. Most of the deviated Redfield values at both rivers' outlets occurred during the dry period.

The mean total silica (TSi) levels were 77 μmol L^{-1} and 90 μmol L^{-1} at the MR and SR outlets, respectively, where the contributions of dissolved silica ($Si(OH)_4$) exceeded 55%. The levels of $Si(OH)_4$ were generally low in both estuaries and averaged 41 μmol L^{-1} in MR and 51 μmol L^{-1} in SR, but during the wet season, the amounts increased with the river water flows (Fig. 3). There were high $Si(OH)_4$-discharge correlations: $r = 0.62$ and 0.68 in SR and MR, respectively ($p < 0.001$). At the SR outlet, the $Si(OH)_4$:DIN ratio (herein referred to as Si:N) was often low (Si:N < 1 in 76% of samples), with an average value that did not exceed 0.72 (Fig. 4). The Si:N ratio was, however, more elevated in MR waters (1.40), and only 24% of the samples had values < 1. For N:P, most of the low and unbalanced Si:N values occurred during the dry period at the SR outlet (Fig. 4).

Similar to particulate nitrogen and phosphorus, particulate silica (BSi) displayed a clear seasonal cycle, with exceptionally high values during the dry period that reached 53.54 μmol L^{-1} and 48.56 μmol L^{-1} (1 mg Si-SiO_2 = 35.71 μmol Si-SiO_2) at the SR and MR outlets, respectively (Fig. 3).

Overall, the BSi concentrations were found to be remarkably elevated throughout the year, even in winter, which was generally the lowest productive period of the year. In addition, it can be noted that the BSi concentrations were largely comparable to the dissolved inorganic form values, and the ratio $Si(OH)_4$:BSi was not much different from unity (1.10 and 1.25 in MR and SR waters, respectively). Nearly half of the available dissolved silica would be converted in the form of particulate silica as diatoms frustules. There were in fact significant correlations between the Chl *a* and BSi concentrations in the two rivers' waters ($r = 0.55$ and 0.62 for SR and MR, respectively; $p < 0.001$). $Si(OH)_4$ amounts however were negatively correlated ($r = -0.35$, $p = 0.01$) with BSi due to their opposite seasonal cycles (Fig. 3) in MR waters, but that correlation became positive in the dry period for the SR waters. Although the Si:N ratio did not exceed unity in most cases in both rivers, the ratio of the organic form BSi:PON displayed high values of approximately 27 and 20 in SR and MR waters, respectively.

The two rivers showed high Chlorophyll *a* amounts, particularly during the warm and dry period (34 and 15 μg L^{-1} for SR and MR, respectively). The phytoplankton biomasses peaked in May and September, consecutive to the decline in river flow (SR) or during the closing period (MR) and to the high NH_4 and PO_4 loads during summertime, as previously described (Fig. 3). The SR waters always experienced large Chl *a* concentrations, which averaged 21 μg L^{-1}, in comparison to those of MR, which were approximately 12 μg L^{-1}. Diatom populations may have represented 10% of the total phytoplankton community because the ratio BSi:Chl *a* was generally approximately 0.1 in MR and 0.05–0.11 in SR (Fig. 4). During the dry period, diatoms may have represented only 5% (BSi:Chl *a* = 0.05, g:g) of the community in SR waters.

Unlike the phytoplankton biomasses, the values of POC were

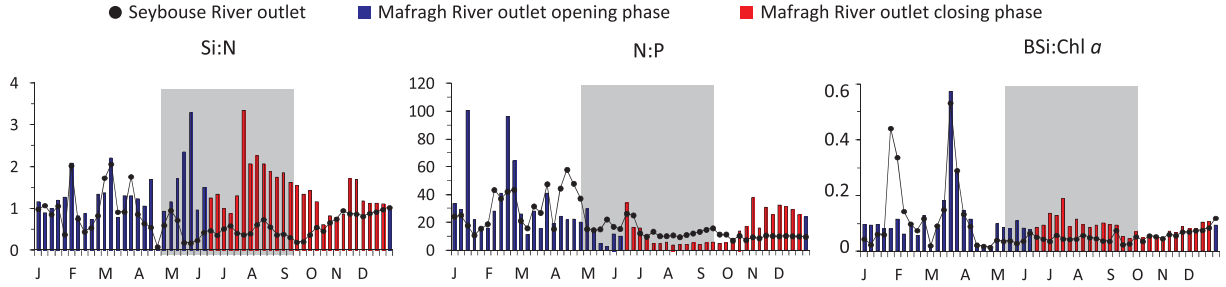

Fig. 4. Si:N; N:P molar ratios, and BSi:Chl *a* (weight ratio: g:g) at the Mafragh and Seybouse River outlets during 2014. The gray area represents the dry season. Mafragh River outlet closing phase: the river outlet was closed from its marine tidal connection from 12 June-21 December 2014; Mafragh River outlet opening phase: the river outlet was opened to sea from 01 January-11 June and from 22 to 30 December 2014.

comparable (800 μmol L^{-1}) in both estuaries and had the same seasonal variation, with maximum values during the dry period (Fig. 3). The POC levels had large and significant correlations with the phytoplankton biomasses ($r = 0.64$ and 0.70 for MR and SR waters, respectively; $p < 0.001$). In addition, the POC:Chl *a* weight ratios (g:g) displayed very high values in both estuaries and varied from 100 to 2100, with averages of 648 at SR and 1089 at MR. Those exceptionally high values may have been related to the advanced rates of phytoplankton standing stock degradation in such highly dynamic estuarine systems. The minimum POC:Chl *a* value occurred during the blooming period (Fig. 3). The BSi was, on average, between 10 and 18.8% (weight ratio in g:g) of the POC concentration, and its fraction increased in the wet period, particularly at the SR outlet. In addition, POC was a main component of SPM, representing 32–45% in the dry period and approximately 20% in the wet period. Because the rivers' outlets are highly productive, particulate organic matter constituted a relevant fraction of SPM. However, there was a negative correlation between POC and SPM ($r = -0.33$ and $p < 0.01$ in SR, and $r = -0.43$ and $p < 0.001$ in MR) and between POC and water flow ($r = -0.61$ and $p < 0.001$ in SR, and $r = -0.57$ and $p < 0.001$in MR). This was because river flow and SPM increased during the wet period in contrast to POC, which was mainly produced during the dry period.

3.3. Nutrient levels in rainwater

The year 2014 was relatively dry, and the precipitation was < 600 mm. The rainfall amounts of 36% of the 100 rainy days in 2014 were < 2 mm (Fig. 5). The rainiest months were December (170.5 mm) and March (153 mm), which together provided more than half the precipitation yield in that year.

The dissolved nutrient seasonal variations are shown in Fig. 5. Overall, the precipitation over Annaba Bay was highly charged with Si $(OH)_4$ and PO_4 (Fig. 5), which respectively amounted to 16.70 and 1.54 μmol L^{-1}. However, the concentrations of nitrogen compounds displayed low values; the TDN average value did not exceed 40.5 μmol L^{-1}, of which NO_3, NH_4 and DON represented 45%, 28.4% and 20%, respectively. The DIN concentration increased by 10% during the dry period, but PO_4 and $Si(OH)_4$ displayed high levels, increasing by 64% and 21%, respectively, over the values in the wet period (Fig. 5). Apart from PO_4, all nutrients had maximum concentrations during summer, in particular NO_3 (28 μmol L^{-1}), DON (17.3 μmol L^{-1}), Si $(OH)_4$ (22.9 μmol L^{-1}) and NH_4 (21.9 μmol L^{-1}). In addition, with the exception of NH_4 and NO_2, all the nutrients dropped to their lowest values during winter (Fig. 5). Moreover, low rainfall days were generally heavily charged with dissolved nutrients in comparison to high rainfall days. However, several rainwater samples from spring and autumn had high concentrations of $Si(OH)_4$ and PO_4 (Fig. 5).

The average N:P ratio (30) was not much different from that of the riverine waters, but only 37% of the samples were situated within the range 8 > N:P < 30. The average value of Si:N (0.66) was found to be remarkably comparable to that of the SR waters. Moreover, almost all samples, with the exception of 4 of them, showed low Si:N (< 1).

3.4. Riverine and atmospheric loading of dissolved and particulate materials

Table 2, compares the fluxes of the various dissolved and particulate materials from riverine and atmospheric sources. The N:P ratios in the atmospheric inputs (~10) were remarkably comparable to those of the riverine inputs, and the Si:N ratio reached 0.5 under wet atmospheric deposition (WAD). This shows the strong dominance of P and Si relative to N in the WAD over the Annaba area. Indeed, the WAD over the Annaba area was characterized by a low DIN flux (14.4 mmol m^{-2} yr^{-1}) but high fluxes of $Si(OH)_4$ (8.1 mmol m^{-2} yr^{-1}) and $P\text{-}PO_4$ (0.88 mmol m^{-2} yr^{-1}).

Together, MR and SR delivered 797 × 10^3 kg yr^{-1} of TN during 2014, of which TDN contributed 95.76% (Table 2). That amount of TDN was 7.6-fold the WAD (99.8 × 10^3 kg yr^{-1}) into Annaba Bay (Table 2). The DIN was the major component of TDN for both atmospheric depositions (80.1%) and riverine (89.2%) inputs when compared to the DON fraction (Table 2). Within the DIN form, $N\text{-}NO_3$ was the major component in the WAD (65.4%) and riverine (65.7%) inputs. That oxidized nitrogen form dominated (67.7%) the TN mass delivered from the MR outlet. However, the $N\text{-}NH_4$ flux was half the $N\text{-}NO_3$ flux in the WAD, with only 3.92 mmol m^{-2} yr^{-1} (Table 2). This flux was 8-fold lower than the riverine flux. Compared to the MR inputs, rainwater was an important source of DON (19.2 × 10^3 kg yr^{-1}) entering Annaba Bay and represented 43% of the sum of the MR and SR inputs.

SR and MR delivered together 237.4 × 10^3 kg yr^{-1} of TP (Table 2), from which the TDP constituted an important fraction (65.8%). Annaba Bay received 112 × 10^3 kg yr^{-1} of DIP, and the two rivers contributed nearly equally to both $P\text{-}PO_4$ and DOP inputs (Table 2). The riverine inputs of $P\text{-}PO_4$ (10.9 × 10^3 kg yr^{-1}) were approximately 7-fold higher than the atmospheric deposition (Table 2). However, the WAD over the Annaba area was heavily charged with $P\text{-}PO_4$ (8.8 mmol m^{-2} yr^{-1}). This may be related to the high dust load from Saharan airflow, which generally crosses North Africa between March and October.

In contrast to PON, POP represented the major fraction within TP components (Table 2), contributing 34.2% on average. MR and SR delivered 2413 × 10^3 kg yr^{-1} of total silica (TSi), of which 68.9% was in the form of dissolved silica ($Si\text{-}Si(OH)_4$), and delivered 750 × 10^3 kg yr^{-1} of particulate biogenic silica (Si-BSi). In contrast to the nitrogen and phosphorus river deliveries, WAD was 18-fold lower than the river input in terms of $Si\text{-}Si(OH)_4$. Similar to particulate biogenic silica, the two rivers discharged large amounts of POC (4482 × 10^3 kg yr^{-1}), and MR extrusions formed 62.5% of the annual POC input. The BSi:POC loading ratio was approximately 0.1–0.2, depending on the river. The rivers delivered important and approximately equal phytoplankton biomasses (5.8 × 10^3 kg yr^{-1} in total) into Annaba Bay. At the riverine outlets, the sediment yields were not elevated (7.5 and 16.7 × 10^3 kg SPM km^{-2} yr^{-1} for SR and MR, respectively). Not only did the lower catchments act as sedimentary basins, trapping sediments, but the many dry months of 2014 also most probably contributed to the reductions in sediment discharges. Only 3.4–5.2% of the SPM flux was in the form of POC (Table 2).

4. Discussion

4.1. River water quality and dissolved nutrients delivery

The main objective of this work is to assess the relative contributions of riverine and wet atmospheric inputs of materials into the Annaba area during the relatively dry year of 2014. Because of the unusually extended dry period (April-November) of 2014, the MR and SR catchment outlets together delivered into Annaba Bay a small freshwater volume as low as 0.84 × 10^9 m^3. Compared to the mean value of river basins worldwide (Treguer et al., 1995; Conley, 1997), the levels of $Si(OH)_4$ in MR and SR were 3.5-fold lower. Not only is this impoverishment due to reservoir retention (Meybeck and Vörösmarty, 2005; Humborg et al., 2006; Avilés and Niell, 2007; Ounissi and Bouchareb, 2013), but estuarine buffering can also be relevant (Canton et al., 2012; Hallas and Huettel, 2013). The lowering of $Si(OH)_4$ concentrations and the Si:N ratio in SR waters and to a lesser degree in MR waters would have resulted in the lowering of diatom fractions (BSi:Chl *a*: nearly 0.10) within phytoplankton communities. In contrast, PO_4 and NH_4 concentrations at SR in particular remain elevated compared to the major Mediterranean rivers, where those nutrients are decreasing (Ludwig et al., 2010; UNEP/MAP, 2013). The SR water remained disturbed, as the N:P molar ratio was unbalanced with regards to the Redfield ratio in as much as 78% of samples. This disturbance was expressed more through the very low values of Si:N, which were mostly < 1. In contrast to SR, MR appears to function as a nearly pristine estuary, with low nutrient supplies and more balanced Redfield

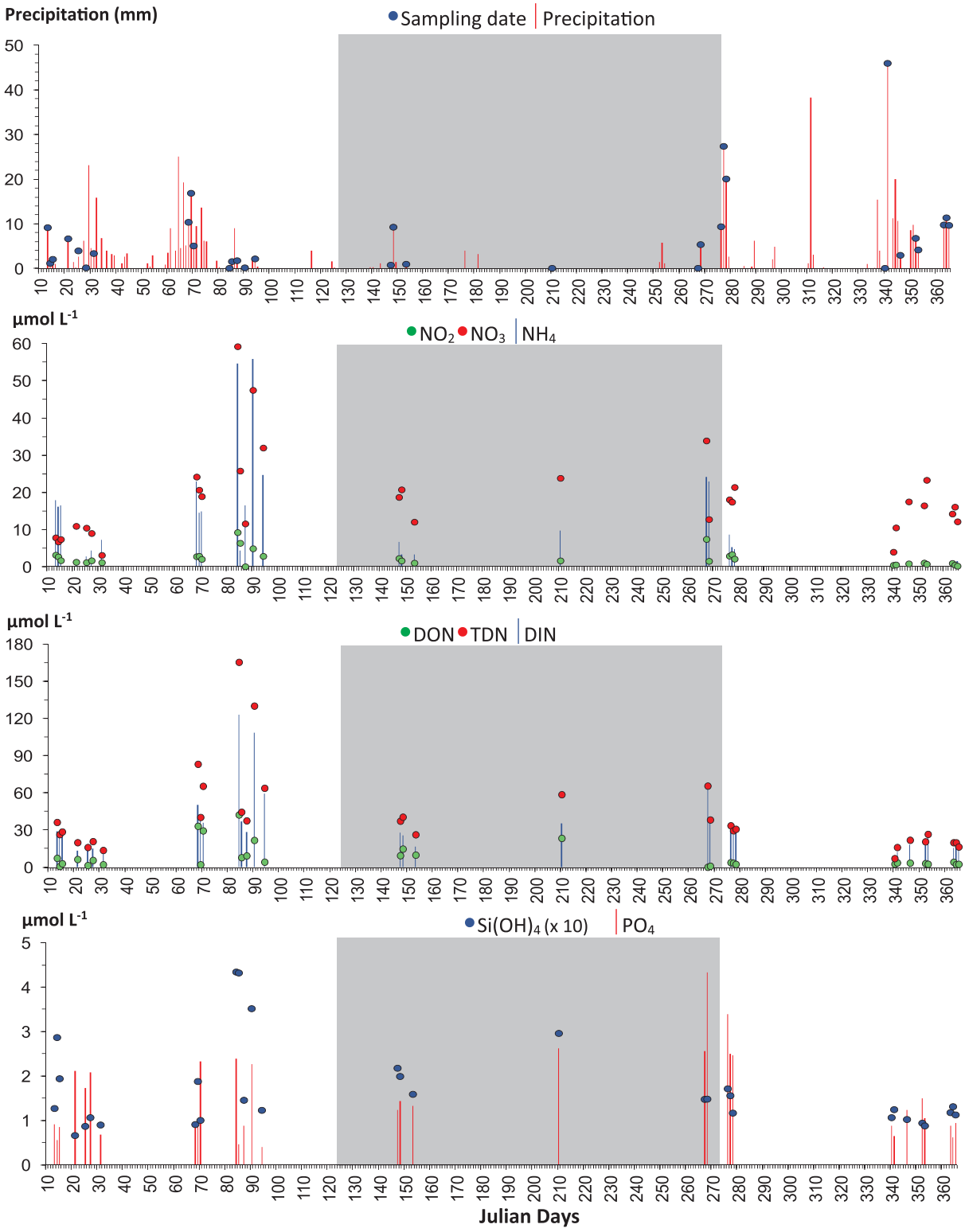

Fig. 5. Seasonal variations in precipitation (top) and nutrient levels in the wet atmospheric deposition samples in 2014. The gray area represents the dry season.

ratios, as has been previously reported (Khélifi-Touhami et al., 2006; Ounissi et al., 2014; Ounissi et al., 2016). Not only have DIN levels increased in most Mediterranean rivers (Ludwig et al., 2010), but silicon concentrations have also markedly decreased due to silicon retention behind dams (Conley et al., 2000; Humborg et al., 2000; Ounissi and Bouchareb, 2013). Particularly the reviews of Billen and Garnier (2007) and Durrieu de Madron et al. (2011) showed a very low Si:N ratio (often < 1) for most European and Mediterranean Rivers. DON and DOP have been recognized as important components within respective N (Berman and bronk, 2003; Pitta et al., 2014; Zhang et al., 2015) and P (Karl and Bjorkman, 2001; Rinker and Powell, 2006; Pitta et al., 2014) pools and generally contribute more than 20% of the total dissolved forms. These dissolved organic forms may provide a significant fraction of N or P demands during dinoflagellate blooms

Table 2
Annual fluxes (kg yr^{-1} and mmol yr^{-1}) of various dissolved and particulate materials from riverine and atmospheric sources estimated for 2014. Specific fluxes (kg km^{-2} yr^{-1}) are in parentheses. AA: Annaba area. AB: Annaba Bay, for which the wet atmospheric deposition has been converted to 10^3 kg yr^{-1} by multiplying the flux over AA (mmol m^{-2} yr^{-1}) by its surface area (400 km^2).

	Rivers						Wet atmospheric deposition		Ratio
	SR		MR		SR + MR		AB	AA	SR + MR/AB
	10^3 kg yr^{-1}	10^6 mmol yr^{-1}	10^3 kg yr^{-1}	10^6 mmol yr^{-1}	10^3 kg yr^{-1}	10^6 mmol yr^{-1}	10^3 kg yr^{-1}	mmol m^{-2} yr^{-1}	
NH_4	121 (18.6)	8.64	66.7 (20.8)	4.76	187.7	13.4	21.9	3.92	8.50
NO_2	38.8 (6)	2.77	17.1 (5.3)	1.22	55.9	4.0	5.9	1.07	9.30
NO_3	217 (33.4)	15.5	249.8 (78.0)	17.84	467	33.4	52.7	9.50	8.86
DIN	377 (58.6)	26.93	333.5 (104.2)	23.82	711	50.7	80.7	14.40	8.81
DON	29.9 (4.6)	2.14	21.8 (6.8)	1.56	51.7	3.64	19.2	3.43	2.70
TDN	407 (62.6)	29.07	355.4 (111.1)	25.40	762.6	54.5	99.8	17.83	7.60
PON	21.1 (3.2)	1.51	13.4 (4.2)	0.96	34.5	2.46			
TN	428 (65.9)	35.07	368.8 (115.2)	26.34	797	61.4			
PO_4	40.9 (6.3)	1.32	31.9 (10.0)	1.03	72.8	2.35	10.88	0.88	6.70
P_2O_5	21.1 (3.2)	0.68	18.2 (5.7)	0.59	39.3	1.27			
DIP	62 (9.5)	2.0	50.1 (15.7)	1.62	112.1	3.62			
DOP	21.9 (3.4)	0.71	22.3 (6.9)	0.72	44.2	1.42			
TDP	83.9 (12.9)	2.71	72.4 (22.6)	2.30	156.2	5.0			
POP	43.7 (6.7)	1.41	37.4 (11.7)	1.21	81.1	2.62			
TP	127.6 (19.6)	4.12	109.8 (34.3)	3.54	237.4	7.7			
$Si(OH)_4$	840 (129.4)	30.0	823 (257.2)	29.40	1663	59.4	90.67	8.10	18.30
BSi	355.4 (54.7)	12.69	394 (123.2	14.1	749.6	26.8			
TSi	1195 (183)	41.6	1217 (380)	43.50	2413	85.0			
POC	1679 (258.4)	148.3	2802 (875.7)	233.5	4482	381.8			
Chl *a*	2.8 (0.4)	0.003	3 (0.9)	0.003	5.8	0.006			
SPM	48,962 (75000)		53,433 (167000)		102,395				

(Mortazavi et al., 2000; Rinker and Powell, 2006; Zhang et al., 2015). DON is seldom considered in routine surveys of water quality (Berman and Bronk, 2003) and is particularly weakly documented for Mediterranean rivers and estuaries (UNEP/MAP, 2013; Pitta et al., 2014). The concentrations and fractions of DON in MR and SR are comparable to most Mediterranean rivers (Pitta et al., 2014). In the two rivers, the DON maximum concentration occurred during spring (44–68 μmol L^{-1}) and summer (13–32 μmol L^{-1}), coinciding with increasing phytoplankton biomass, as reported in Bronk et al. (2007). Because of the indirect DOP measurements, its concentration was apparently overestimated, and the average values reached 2 and 4 μmol L^{-1} in MR and SR, respectively. Those values are not much different from, for example, those of the Evros River, Greece (Pitta et al., 2014), Ebro River (Artigas et al., 2012), Delaware estuary (Volk et al., 2012), and Mississippi River (Rinker and Powell, 2006).

The river flow reductions during most of 2014 resulted in very low fluxes of all dissolved nutrients. In addition, the dissolved nutrient deliveries from the SR and MR catchments (Ounissi et al., 2014) were found to be 2.5–6 higher in wet years (2007 and 2009) than those in dry years such as 2014. MR fluxes of all dissolved nutrients, when compared to those of SR, which is usually considered to be the most developed catchment, was the most important (Ounissi et al., 2014). The SR and MR catchments delivered 58.6–104.2 kg km^{-2} yr^{-1} of DIN, 6.3–10 kg km^{-2} yr^{-1}, 6.8–4.6 kg km^{-2} yr^{-1} of DON, P-PO_4, 129.4–257 kg km^{-2} yr^{-1} of Si-$Si(OH)_4$, respectively. These loads are very low especially for Si-$Si(OH)_4$ when compared to those of most Mediterranean rivers (Table 3). These reduced fluxes are mainly due the low river flow into the North African Mediterranean coasts.

4.2. Riverine particulate materials delivery

Not only the smaller river flows during 2014 significantly reduced the sediment loads (75 and 167 t km^{-2} yr^{-1} for Mafragh and Seybouse respectively), but dams probably trapped more than 70% of the incoming sediment masses, as observed in many contiguous Algerian river catchments (Ounissi and Bouchareb, 2013; Taamallah et al., 2016). Mean sediment yield of 61 t km^{-2} yr^{-1} has been reported by Meybeck and Moatar (2012) for 86 river catchments of semi-arid and temperate regions. The sediment yield for Mediterranean rivers is around 580 t km^{-2} yr^{-1}, but because of the considerable dam building,

Table 3
Specific fluxes (kg km^{-2} yr^{-1}) of nutrients from selected Mediterranean coastal rivers.

Rivers	NH_4	NO_3	DIN	DON	PO_4	$Si(OH)_4$	References
Axios, Greece			952		665.2	1972	El Boukhary (2005)
Aliakmon, Greece			782		106.2	2638	El Boukhary (2005)
Gallikos, Greece			850		37	2550	El Boukhary (2005)
Pinios, Greece			1163		175	3489	El Boukhary (2005)
Pinios, Greece	180	496	700		166		UNEP/MAP (2013)
Têt, France	383	331	756	184	34		UNEP/MAP (2013)
Ter, Spain	24.3	314	350	41.9	15.4		UNEP/MAP (2013)
Ebro, Spain	4.4	146	152.7		2	140	Falco et al. (2010)
Adige, Italy	39.7	556	605	159	24.8		UNEP/MAP (2013)
Po, Italy	58.2	1520	1590	1290	45.2		UNEP/MAP (2013)
Rhone, France	38.4	816	866		27.4		UNEP/MAP (2013)
Reno, Italy	91.5	385	486	187	19.3		UNEP/MAP (2013)
Argens, France	11.3	213	230	88.7	11.3		UNEP/MAP (2013)
Herault, France	23.3	221	248		7.76		UNEP/MAP (2013)
Krka, Croatia	1.81	201	215	90.3	5.46		UNEP/MAP (2013)
Neretva, Croatia	24.3	623	643	241	5.3		UNEP/MAP (2013)
Gediz, Turkey	190	96.4	304		36.8		UNEP/MAP (2013)
Seyhan, Turkey	94	556	744		74.4		UNEP/MAP (2013)
Ceyhan, Turkey	94.7	536	650		29.9		UNEP/MAP (2013)
Kebir-Rhumel, Algeria	12	17	31	13	10	111	Ounissi and Bouchareb (2013)
Kebir West, Algeria	85	92	222	112	88	1117	Ounissi and Bouchareb (2013)
Saf-Saf, Algeria	136	132	296	42	58	2694	Ounissi and Bouchareb (2013)
Seybouse, Algeria	300	47.5	359		8.5	403	Ounissi et al. (2014)
Mafragh, Algeria	44	53	111		15	543	Ounissi et al. (2014)
Evros, Greece	2.40	11.1	13.46	3.57	1.49		Pitta et al. (2014)
Mafragh (MR), Algeria	20.8	78	104.2	4.6	10	257.2	This study
Seybouse (SR), Algeria	18.6	33.4	58.6	6.8	6.3	129.4	This study

the actual sediment flux is reduced to 251 t km^{-2} yr^{-1} (UNEP/MAP, 2003). More recently Sadaoui et al. (2017) reported sediment retention by dams of 35%, corresponding to 137 t km^{-2} yr^{-1} sediment yield.

The Chl *a* levels were high during the dry period, as for many Mediterranean river outlets (among others, the Ebro River by Sabater et al., 2008, the Pô River by Berto et al., 2010, the Guadiana River by Domingues et al., 2011 and the Moulouya River by Tovar-Sánchez et al., 2016). The high Chl *a* biomass at the SR outlet may be linked to the development of non-siliceous and harmful phytoplankton taxa. If we assume that the entirety of BSi is due to diatom growth and non-living frustules, it may represent only 8–10% of Chl *a* biomass, depending on the river. Those low BSi fractions (or diatom contents) may imply that large non-siliceous phytoplankton taxa dominated the rivers' waters. However, BSi concentrations from MR and SR were 1.5 times the mean (28 µmol L^{-1}) of rivers worldwide (Conley, 1997). This also results in a very high amount of POC, which represented, for example, 3 to 6-fold increases in the mean concentrations of the rivers discharging into the North Mediterranean Sea (e.g., Tockner et al., 2009; Bizsel et al., 2011; Cozzi and Giani, 2011; Higueras et al., 2014). However, the PON concentration was still rather low (4.4–9 µmol L^{-1}) in comparison to other Mediterranean rivers (Moutin et al., 1998; Ludwig et al., 2009; Tockner et al., 2009; Higueras et al., 2014).

Unlike the dissolved inorganic nutrients, the organic and particulate matter fluxes displayed high values, particularly the POC, POP, Chl *a* and BSi derived from the MR catchment. The POC yield reached 258–875 kg km^{-2} yr^{-1} for SR and MR deliveries, respectively. Yet these topsoil losses remain very low compared to the most Mediterranean catchments (e.g. Higueras et al., 2014). Similarly, the BSi yield of MR dominated the deliveries into Annaba Bay and represented 31% of TSi. Within TSi, BSi accounted for about 30% in the SR and MR waters. For the large world rivers, Conley (1997) reported a BSi:TSi ratio varying in the range of 7–41% and a BSi specific flux of 28–17192 kg km^{-2} yr^{-1}. The contribution of BSi carried by rivers to the world ocean has been recognized (Conley, 1997; Garnier et al., 2002; Tréguer et al., 1995), and as potential bioavailable stock (after dissolution) should be considered in silicon budgets and cycling (Billen and Garnier, 2007; Tréguer and De La Rocha, 2013).

4.3. Atmospheric wet deposition of nutrient inputs

Atmospheric deposition is a significant source of nutrients entering the Mediterranean Sea (Koçak et al., 2010; Christodoulaki et al., 2013; Im et al., 2013; Richon et al., 2017), as river discharge and nutrient fluxes have decreased due to dams retention and climate change (Humborg et al., 2000; Ludwig et al., 2009; Lehner et al., 2011). Rainwater in the Annaba region is characterized by high $Si(OH)_4$ and PO_4 concentration in comparison to other Mediterranean sites (Herut et al., 1999; Mace et al., 2003; Markaki et al., 2003; Chen et al., 2007; Koçak et al., 2010; Izquierdo and Avila, 2012; Violaki et al., 2017). $Si(OH)_4$ and PO_4 levels increased during the dry period, when airflow originating from the Algerian desert was predominant. Koçak et al. (2010) found a comparable Saharan dust load effect for the northeast Mediterranean Sea. The WAD of DIN and DON over the Annaba area were oppositely among the lowest in the Mediterranean region (e.g., Mace et al., 2003; Chen et al., 2007; Koçak et al., 2010; Violaki et al., 2010; Izquierdo and Avila, 2012). Although the abundance of TDN on the northern Mediterranean side can be related to polluted airflow from Europe (Mace et al., 2003; Koçak et al., 2010; Richon et al., 2017), the low depositions of TDN components may be due to the relatively low human activities (agriculture, transportation and industries) in the Annaba region and to the washout of European air masses before reaching North Africa.

Similar to most Mediterranean coastal sites (Table 4), the DON flux in Annaba rainwater contributed significantly to the TDN pool and represented 20% (Table 4). The main particularity of the Annaba atmosphere is the strong wet depositions of Si-$Si(OH)_4$ and P-PO_4, which are 3–12-fold and 2.5-fold the average Mediterranean values, respectively (Table 4). These high deposition fluxes may be related to eolian Saharan dust exported from North Africa (Moulin et al., 1998; Tréguer and De La Rocha, 2013; Varga et al., 2014; Koçak, 2015; Gkikas et al., 2016; Richon et al., 2017) and partially to local anthropogenic dust injection. In contrast, and because of the low human activities, the DON and DIN fluxes were three times lower than the average values for the Mediterranean region (Table 4).

Obviously the atmospheric contribution derived from wet deposition sampling in this work is clearly underestimated because the study region is also exposed to atmospheric dry deposition of Saharan dust that we did not sample. From weekly samplings of insoluble atmospheric deposition monitored at Lampedusa Island (35.52°N, 12.63°E, approximately 460 km ESE from Annaba), Vincent et al. (2016) report that dry deposition accounted for 46% of the total dust deposition associated with the 37 most intense deposition events observed from September 2011 to December 2013, which themselves accounted for 84% of the total dust deposition recorded over the period.

4.4. Atmospheric deposition versus riverine nutrient inputs

In addition to evaluating the relative importance of the dissolved and particulate matter inputs into Annaba Bay across the MR and SR outlets, this study also assessed the relative contributions of riverine and wet atmospheric inputs of dissolved nutrients into Annaba Bay. The

Table 4
Specific fluxes (mmol m^{-2} yr^{-1}) of nutrients from wet atmospheric deposition over selected Mediterranean coastal area.

Site	NH_4	NO_3	DIN	DON	PO_4	$Si(OH)_4$	Source
Cap Ferrat, France			50		0.37		Migon et al. (1989)
Corsica					0.43[a]	00–6.7	Tréguer et al. (1995)
Northern Israel coast			23.9		0.23	–	Herut and Krom (1996)
South East Mediterranean			28.5		0.21		Herut and Krom (1996)
Tel shikmona, Israel	13	20	33		0.3		Herut et al. (1999)
Ashdod, Israel	19.2	6.9	26		0.2		Herut et al. (1999)
Heraklion, Crete			24				Kouvarakis et al. (2001)
Finokalia, Crete			17				Kouvarakis et al. (2001)
Erdemli, Turkey		16	–				Markaki et al. (2003)
Heraklion, Crete	11	9	20		0.7		Markaki et al. (2003)
Erdemli, Turkey	23	22	45		0.34	0.92	Koçak et al. (2010)
Erdemli, Turkey [b]	16	13	29		0.18	0.54	Koçak et al. (2010)
Erdemli, Turkey[c]	7	9	16		0.16	0.38	Koçak et al. (2010)
Cap Spartel, Morocco			28.2		0.7		Markaki et al. (2010)
Cap Bear, France			45.9		0.6		Markaki et al. (2010)
Ostriconi, France			25.4		0.5		Markaki et al. (2010)
Mahdia, Tunisia			18.1		0.4		Markaki et al. (2010)
Gozo, Malta			46.1		0.4		Markaki et al. (2010)
Finokalia, Greece			39.1		0.2		Markaki et al. (2010)
Mytilene, Greece			28.9		0.3		Markaki et al. (2010)
Alexandria, Egypt			77.9		0.5		Markaki et al. (2010)
Cavo Greco, Cyprus			47.7		0.5		Markaki et al. (2010)
Akkuyu, Turkey			30,6		0.4		Markaki et al. (2010)
Finokalia, Crete	31.6	45.7	77.3	22.7			Violaki et al. (2010)
Zmiinyi Island, Ukraine	13.4	10.2	23.2		0.97		Medinets and Medinets (2012)
La Castanya, NE Spain	26.5	17.3					Izquierdo and Avila (2012)
Cap Ferrat, France			35		0.11		De Fommervault et al. (2015)
Erdemli, Turkey	22.6	21.9	44.5		0.33	0.91	Koçak et al. (2015)
Sinop, Turkey	0.7	2.2	2.9		0.27		Koçak et al. (2016)
Finokalia, Crete					0.6		Violaki et al. (2017)
Frioul Island, France				11.9			Djaoudi et al. (2017)
Erdemli, Turkey	14.3	11.7	26	10.7			Nehir and Koçak (2017)
Annaba, Algeria	3.9	9.5	14.4	3.4	0.9	9.10	This study

[a] Bergametti et al. (1992).
[b] Winter.
[c] Spring and autumn.

riverine inputs were found to be the main source of dissolved nutrients entering Annaba Bay. They were 8.8-fold, 6.7-fold, 2.7-fold and 18-fold the atmospheric fluxes of DIN, P-PO_4, DON and Si-$Si(OH)_4$, respectively. The superiority of atmospheric deposition over river inputs has been reported in the northeast Mediterranean region (Koçak et al., 2010) for DIN and P-PO_4, but rivers input of S-$Si(OH)_4$ were 10-fold those of rainwater. However, estimates by Martin et al. (1989) showed that DIN river inputs were just comparable to rainwater and that phosphorus loads primarily originated from river runoff. Moreover, the review of Durrieu de Madron et al. (2011) reported that atmospheric deposition can be the main external nutrient supply (Bartoli et al., 2005; Guieu et al., 2010) for the Mediterranean open waters, and more importantly episodes of Saharan dust deposition can enhance the primary production (Ridame and Guieu, 2002; Bonnet et al., 2005; Guieu et al., 2014). As a consequence of the high dust load from the Algerian desert, the rainwater over the Annaba coastal area is heavily loaded with phosphate and silicate compared to other Mediterranean regions (e.g., Herut et al., 1999; Markaki et al., 2003, 2010; Koçak et al., 2010). In addition, because of the abundance of both phosphorus and silicon in rainwater, the Redfield ratios are not far from those of the rivers but are very different from the ratios in Mediterranean rainwater reported by Herut et al. (1999), Markaki et al. (2003, 2010), Koçak et al. (2010) and Durrieu de Madron et al. (2011).

Table 5 provides the nutrient fluxes from both riverine and atmospheric sources for different world ecosystems, and shows large variability between rivers and atmospheres flux and contribution. For instance, the riverine loads of DIN may vary from 5.8 mmol m^{-2} yr^{-1} in the Yellow Sea to 195 mmol m^{-2} yr^{-1} in the Black sea; 0.27 mmol DIP m^{-2} yr^{-1} in East China Sea to 5 mmol DIP m^{-2} yr^{-1} in the Black sea; 14 mmol DSi m^{-2} yr^{-1} in the Western Mediterranean to 173 mmol DSi m^{-2} yr^{-1} in the Southern yellow Sea.

As shown in table 5, most of these marine systems receive more DIN from atmospheric deposition than river inputs. However, the black Sea, Southern Yellow Sea, East China Sea and North sea showed the dominance of river input over the atmospheric one (Table 5). At the opposite, rivers are the dominant source of DIP and DSi inputs in most Mediterranean and world marine areas, as can be seen in Table 5.

As for riverine inputs, there is a strong variability of atmospheric nutrient supplies over the ocean world. In rainwater DIN flux varied between 2.9 mmol m^{-2} yr^{-1} in Sinop to 500 mmol m^{-2} yr^{-1} in the Baltic Sea; 0.07 mmol DIP m^{-2} yr^{-1} in Heraklion to 4 mmol DIP m^{-2} yr^{-1} in the West Mediterranean; 0.78 mmol DSi m^{-2} yr^{-1} in the East Mediterranean to 9.1 mmol DSi m^{-2} yr^{-1} in the Annaba area, SW Mediterranean. This high atmospheric deposition variability of nutrients resulted in differential primary production. Atmospheric deposition of nitrogen can account for 35–60% of new production in the Mediterranean Sea (Christodoulaki et al., 2013), up to 5% in the black Sea (Koçak et al., 2016) and up to 9.2% in the Yellow Sea (Zou et al., 2000). According to Violaki et al. (2017), atmospheric deposition of phosphorus can sustain 14 and 38% of new production in the NW Mediterranean and the Eastern Mediterranean during the oligotrophic period, respectively. However, the phosphorus deposition can enhance the primary production by 5% in the eutrophic black Sea (Koçak et al., 2016) and sustain 38% in the SE Mediterranean (Markaki et al., 2003).

It is clear that rainwater represents a relevant source of fertilizers to marine waters and agricultural land in the Annaba area and can compensate for the loss of nutrients due to dam retention and soil erosion in coastal catchments. Future studies including wet and dry atmospheric and riverine inputs of dissolved and particulate matter will provide a clear picture on the Mediterranean Sea atmosphere-land interactions.

Table 5
Riverine versus atmospheric inputs (mmol m^{-2} yr^{-1}) of nutrients for different world marine ecosystems.

	NH_4	NO_3	DIN	DIP	$Si(OH)_4$	Reference
				Western Mediterranean		
Western Mediterranean			33	4.0		Martin et al. (1989)
Cap Ferrat, France			52	0.37		Migon et al. (1989)
Capo Cavallo, Corsica				0.43		Bergametti et al. (1992)
Corsica					0.0–6.7	Tréguer et al. (1995)
Annaba, Algeria	3.9	9.5	14.4	0.9	9.1	This study
Cap Ferrat, France			35	0.11		De Fommervault et al. (2015)
Riverine			34.3	5.5		UNEP (1984)
Riverine			21	1	15	Ludwig et al. (2009)
				Eastern Mediterranean		
Wet atmos. Deposition						
Tel Shikmona, Israel	13	20	33	0.3		Herut et al. (1999)
Heraklion, Crete	11	9	20	0.07		Markaki et al. (2003)
Erdemli, Turkey	23	22	45	0.92	0.92	Koçak et al. (2010)
Atmos. Deposition						
Tel Shikmona, Israel	24	40	64	0.81		Herut et al. (1999, 2002)
Finokalia, Crete	13	19	32	0.15		Markaki et al. (2003)
Erdemli, Turkey	26	44	70	1.14	1.46	Koçak et al. (2010)
Eastern Mediterranean					0.78	Krom et al. (2014)
Riverine			21	1	14	Ludwig et al. (2009)
				Mediterranean		
Atmos. Deposition			31.97	0.90		Guerzoni et al. (1999)
Riverine			28.75	1.88		Guerzoni et al. (1999)
				Black Sea		
Wet atmos. deposition						
Western Black Sea	13	10.2	23.2	0.97		Medinets and Medinets (2012)
Sinop, Turkey	0.7	2.2	2.9	0.27		Koçak et al. (2016)
Atmos. Deposition						
Western Black Sea	31.9	17.5	49.4	3.13		Medinets and Medinets (2012)
Sinop, Turkey	2.1	4.8	6.9	0.54		Koçak et al. (2016)
Varna, Bulgaria	7.8	16.5	24.3	1.66		Koçak et al. (2016)
Riverine			195	5	67	Ludwig et al. (2009)
				Baltic Seas		
Atmos. deposition			500			Voss et al. (2005)
Riverine			157			Voss et al. (2005)
				North Sea		
Atmos. deposition			39			Rendell et al. (1993)
Riverine			100			Rendell et al. (1993)
				Northeast United States		
Atmos. deposition		85.7				Howarth et al. (2002)
Riverine		56.4				Howarth et al. (2002)
				Southern California Bight		
Atmos. deposition [a]	16	25	41			Howard et al. (2014)
Riverine [a]	6	32	38			Howard et al. (2014)
				Yellow Sea and Bohai Sea		
Atmos. deposition			165			Bashkin et al. (2002)
Riverine			5.8			Tong et al. (2015)
				Southern Yellow Sea		
Atmos. deposition	23.8	28.1	52	0.72	2.6	Song (2011)
Riverine	7.7	48.7	57	0.59	173	Song (2011)
				East China Sea		
Atmos. deposition	3.20	14.1	105	0.32	3.42	Song (2011)
Riverine	18.7	24.1	125[b]	0.27	45.7	Song (2011)
				Yellow sea and East of China		
Wet atmos. deposition					2.6	Zhang et al. (2005)
				Sea of Japan		
Atmos. deposition			79			Sugimoto et al. (2017)
Kita River			84			Sugimoto et al. (2017)
Atmos. deposition			79			Sugimoto et al. (2017)
Minami River			56			Sugimoto et al. (2017)

Atmos. deposition: wet + dry atmospheric deposition.

[a] Mean of California Bight coastal waters (Santa Barbara, Ventura, Santa Monica Bay, San Pedro, North San Diego, San Diego) and their respective river basins input.

[b] Tong et al. (2015).

5. Conclusions

This study assessed for the first time the relative contributions of riverine and wet atmospheric inputs of materials into the Annaba area on the Algerian coast based on extensive sampling and chemical analyses (54 river water samples from the Mafragh and Seybouse Rivers and 32 rainwater samples) in the relatively dry year of 2014, as characterized by an unusually dry period from April to November. The wet atmospheric deposition contributed 5–37% of the riverine inputs, depending on the element, and constituted an important source of dissolved nutrients entering Annaba Bay.

Although the DIN and DON levels in the WAD in the Annaba area were among the lowest in the Mediterranean region, the rainwater in the Annaba region was characterized by high levels of $Si(OH)_4$ and PO_4,

which increased during the dry period when high Saharan dust load events occurred with airflows originating over the Algerian desert. This phenomenon resulted in a strong WAD of Si-$Si(OH)_4$ and P-PO_4, which showed 3 to 12-fold and 2.5-fold increases over the average Mediterranean concentrations, respectively.

The decreased riverine discharge during 2014 resulted in low loadings of all dissolved nutrients, whereas the yields of particulate matter (POC, POP, Chl *a* and BSi) displayed high values, especially at the MR catchment's outlet, which could have enriched the receiving coastal waters.

As for the particulate forms of N (NOP) and P (POP), the respective dissolved organic forms (DON and DOP) were found to significantly contribute to the total flux and should thus be considered in N and P budgets and cycling. Those organic forms contributed up to 50% (DOP + POP) and 12% (DON + PON) of their respective total fluxes (TP and TN, respectively). Similarly, at both rivers' outlets, the BSi represented 30–32% of the TaSi riverine flux into Annaba Bay and should be better included in routine monitoring programs.

Although the levels of all materials in MR water were always lower than those in SR, the specific fluxes from MR surpassed by several-fold those of SR, which is usually considered to be the most developed catchment. Considering its high specific flow and water discharge, the MR can be assumed to be the most important river in Algeria. Moreover, the MR water had roughly comparable concentrations of dissolved nutrients (except $Si(OH)_4$) to those of rainwater and appeared to function as a nearly pristine ecosystem, with low nutrient levels and more balanced Redfield ratios.

In SR water, the concentration of $Si(OH)_4$ was 3-fold lower than the mean value of the world's rivers, but the PO_4 and NH_4 concentrations remained elevated when compared to the major Mediterranean rivers, in which those nutrient concentrations are decreasing. The SR waters were thus disturbed, as the N:P and Si:N molar ratios were unbalanced in most samples. Those disturbances might explain not only the large phytoplankton biomass but also the lowering of diatom fractions (BSi:Chl $a \approx 0.10$) and probably the development of non-siliceous phytoplankton species.

However, it seems that rainwater can be a relevant source of fertilizers for agricultural land and open marine waters in the Annaba area and can partially compensate for the loss of $Si(OH)_4$ due to dam retention and soil erosion in the coastal catchments.

Finally, we must emphasize that the atmospheric contribution derived from wet deposition sampling in this work was clearly underestimated because the study region is also exposed to atmospheric dry deposition of Saharan dust.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.pocean.2018.04.001.

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µg L^{-1}: microgram per liter
µmol L^{-1}: Micromol per liter
ANOVA: Analysis of variance
BSi:Chl*a*: Biogenic silica to chloropyll ratio
BSi: Biogenic silica
Chl *a*: Chlorophyll *a*
CO_2: Carbon dioxide
DIN: Dissolved inorganic nitrogen
DIP: Dissolved inorganic phosphorus
DON: Dissolved organic nitrogen
DOP: Dissolved organic phosphorus
mg L^{-1}: milligram per liter
mm: millimeter
MR: Mafragh River
N:P : Nitrogen to phosphorus ratio
N: Nitrogen
NH_4^+: Ammonium ion also noted NH_4
NO_2^-: Nitrite ion also noted NO_2
NO_3^-: Nitrate ion also noted NO_3
P: Phosphorus
p: probability
P_2O_5: Polyphosphates
PO_4^{3-}: Phosphate ion also noted PO_4
POC:Chl*a*: Particulate carbon to chlorophyll ratio
POC: Particulate organic carbon
PON: Particulate organic nitrogen
POP: Particulate organic phosphorus
PSS: Practical Salinity Scale
r: correlation coefficient
$Si(OH)_4$: Silicic acid noted SiO_4
Si:N: Silicon to nitrogen ratio
Si:P:N: standard Redfield ratios of the atomic composition of the water and aquatic organisms
Si: Silicon
$Si(OH)_4$:BSi: Silicate to biogenica silica ratio
SPM: Suspended particulate mater
SR: Seybouse River
Std: standard deviation
TDN: Total dissolved nitrogen
TDP: Total dissolved phosphorus
TN: Total nitrogen
TP: Total phosphorus
TSi: total silica is the sum of dissolved silica (SiO_4) and particulate biogenic silica (BSi) when negalcted the lithogenic silica in estuarine environments
WAD: Wet atmospheric deposition