Marine Pollution Bulletin 156 (2020) 111231

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Transport of nutrients from the Seybouse River to Annaba Bay (Algeria, SW Mediterranean)

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ARTICLE INFO

Keywords:
Nutrients
Si:N:P stoichiometry
River input
Seybouse River estuary
Annaba Bay
Mediterranean Sea

ABSTRACT

Freshwater and dissolved nutrient inputs that entered the lower Seybouse River estuary were assessed in 2012 through a fortnightly surface water sampling both at a lower river station and at the estuary outlet. The Seybouse estuary delivered annually 950 × 10^6 m^3 of freshwater yielding 83 kg N km^{-2} yr^{-1} of N-NH_4 and 12 kg P km^{-2} yr^{-1} of P-PO_4. More than 2/3 of the annual inputs of freshwater, $Si(OH)_4$ and NO_3 entered the sea during the flooding event of late February 2012. Si-$Si(OH)_4$ and N-NO_3 yields in the Seybouse estuary represented < 1/3 those of the Mediterranean rivers. Annaba Bay is subjected to highly polluted waters from the Seybouse estuary, with significant NH_4 (72 ± 37 µmol L^{-1}) and PO_4 (7 ± 4 µmol L^{-1}) amounts. However it is characterized by low $Si(OH)_4$ (104 ± 43 µmol L^{-1}) amounts. Alteration of Si:N:P ratios at this bay suggest potential risk of eutrophication, except during and weeks after flood episodes.

1. Introduction

Estuaries are highly dynamic transition zones between terrestrial freshwater and the sea, receiving considerable amounts of various materials passing from the catchment to the sea (Elliot and McLusky, 2002; Falco et al., 2010; Nedwell et al., 1999; Tappin, 2002). In addition to their high productivity, and ecological and economic values (Nixon et al., 2004), estuaries are critical for nutrient regulation, particulate matter recycling and detoxification of polluted waters (Levin et al., 2001; Lisitzin, 1999; Sharps et al., 2015; Toublanc et al., 2016). However, estuaries are facing severe anthropogenic pressures, being particularly sensitive to human various disturbances including nutrient enrichment, chemical contamination, freshwater diversions, and habitat loss or alteration (Elliot and McLusky, 2002; Kennish, 2002). The functioning and productivity of adjacent coasts are strongly influenced by the quantity and quality of the freshwater delivery. Montagna et al. (2002) noted that nothing is more fundamental to the functioning of an estuary than the quantity and the timing of freshwater inflow. Despite the efforts in riverine nutrient reductions, discharges into coastal waters are increasing due to rising trends in urban population and fertilizer use (Beusen et al., 2016; Moore et al., 2013; Seitzinger et al., 2005; Statham, 2012).

In the Mediterranean rivers, Ludwig et al. (2009) reported that nitrogen (N) and phosphorus (P) inputs to the Mediterranean Sea may have had a several-fold increase. By contrast, the dissolved silica (Si) levels are expected to decrease, due to extensive dam building (Lehner et al., 2011), enhancing Si retention rates (Durr et al., 2009; Humborg et al., 2000). Such human perturbations did not only affect the riverine discharge of dissolved silica, but also led to the decrease of Si:N:P ratios in the receiving coastal waters and the limitation of diatom growth and marine and estuarine phytoplankton composition and productivity (Glibert et al., 2012; Howarth and Marino, 2006; Humborg et al., 2000). Several studies demonstrated how aquatic ecosystems can undergo fundamental food web changes including diatom proliferation if Si:N ratio falls below 1:1, (Justic et al., 1995; Officer and Ryther, 1980; Smayda, 1990; Turner et al., 1998). Billen and Garnier (2007) proposed an indicator of coastal eutrophication (ICEP) to assess the potential of river systems for coastal eutrophication, which is based on Si:N:P ratios and fluxes. The ICEP considers that coastal eutrophication results in the new production of non-siliceous algae (expressed in equivalent carbon biomass) sustained by N and P delivered in excess over dissolved silica, with regard to the requirements for diatom growth. The ICEP has been globally applied to the world's coastal rivers (Garnier et al., 2010) and also to European and Mediterranean coastal rivers (Romero et al.,

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https://doi.org/10.1016/j.marpolbul.2020.111231
Received 21 September 2019; Received in revised form 26 April 2020; Accepted 27 April 2020

2013).

North African coastal rivers are experiencing an exceptional reduction in river flows due to dam storage, extraction for irrigation and climate change (Margat and Treyer, 2004; Ounissi and Bouchareb, 2013; Tovar-Sánchez et al., 2016). Moreover, inadequate treatments of domestic and industrial wastes added to inefficacious urban development plans in North Africa (Kitheka et al., 2009) would have increased pressures on river systems, leading to eutrophication, pollution and aquatic water quality alteration (Tovar-Sánchez et al., 2016). Precipitation in the Mediterranean region is characterized by irregularity and often very stormy patterns (Gaum et al., 2016; Lionello et al., 2014). This resulted in a very small base freshwater flow during the long dry period of April–September and flash flood episodes occurring in autumn-winter, disrupting that nearly null flow conditions. During these flash flood events, freshwater discharge into the sea can be multiplied by a factor of 10, delivering a major fraction of the annual loads of inorganic and organic nutrients plus other materials into the coastal zone (Estrela et al., 2001). In the same context, it has been demonstrated that despite their low magnitude and temporary nature, flash flood events constitute a large fraction of terrestrial material inputs along the Mediterranean coast (Guizien et al., 2007; Tzoraki and Nikolaidis, 2007). This will have evident consequences on the biogeochemical cycling of nutrients as well as on the role of estuaries and coastal areas as buffer zones between terrestrial and marine systems. The other main characteristic of Mediterranean estuaries is both their small portion and small tidal range (Falco et al., 2010; Ibàñez et al., 1997), which makes them very sensitive to heavy rain episodes and wind storm pulses. Their seasonal pattern can consequently be significantly disrupted.

The Seybouse River (165 km length) has a small salt wedge estuary of about 8 km with a micro-tidal and semidiurnal regime (Ounissi et al., 2014, 2018). The extent of this part strongly varies according to the importance of the river flow, and function as an atypical estuary, evolving throughout the year over three phases: river, estuarine and saline lake phases (Ounissi et al., 2014). As the tidal range is very small ($\approx$20 cm), the duration of each phase may strongly vary depending on the river input and the duration of the dry season. During an extended dry period, the estuary's outlet might be nearly closed and disconnected from tidal inlets for several months (saline lake phase). In contrast, during high freshwater input episodes (river phase), often occurring between November–March, the salt wedge could be entirely discharged into the sea. On a wet year the estuary is connected to the sea, being dominated by the tidal intrusion, even during the dry period (April–October). In this dry period, the estuary presents intense vertical stratification (Ounissi et al., 2014, 2018). The extent of the estuarine phase, out of the flood episodes, depends both on dam's retention and direct water abstraction for agricultural needs. Estuarine and saline lake phases are characterized by the accumulation of both endogenous and incoming various materials, but during the river phase the entire water layer (with its accumulated matter) could be driven by the high river discharges up to the adjacent coastal waters. In the Mediterranean, Spanish estuaries present a similar hydrological cycle, which are governed by the tide weakness, precipitation regime and water retention in reservoirs (e.g. Basterretxea et al., 2017; Falco, 2003; Ibàñez et al., 1997; Sierra et al., 2002).

Information on water discharges in North African Rivers is hugely lacking, despite their importance in evaluating anthropogenic pressures on the catchments and the receiving marine coastal waters (Ibàñez and Prat, 2003; Tovar-Sánchez et al., 2016). For example, the most recent complete dataset on the Mediterranean catchments, for nutrient concentrations and water discharges, related to the rivers and to the sea (PERSEUS-UNEP/MAP, 2015), not only omitted the North African rivers discharges (except the Nile River) for the lack of data but assumed them to be close to zero. The database for North Africa is poorly documented (UNEP/MAP, 2013; EEA, 2014), despite the fact that many of these rivers have large water, nutrient, and sediment inputs and are particularly susceptible to natural and anthropogenic changes (McNeill, 2002; Ounissi and Bouchareb, 2013; Ounissi et al., 2018). Also, Tovar-Sánchez et al. (2016) outlined that in northern Africa, information on both river alteration and its effects on the coastal waters is fragmented and mostly gathered in unpublished reports. Very few is known about the role of even the largest North African rivers, namely Moulouya (Morocco), Chéliff (Algeria), Medjerda (Tunisia), which are considered as resources for the economic development of the countries in this region (McNeill, 2002; Probst and Suchet, 1992; Tovar-Sánchez et al., 2016). These significant gaps in the Mediterranean rivers discharges and nutrient inputs prevent a true representation of the global picture of freshwater and nutrient inputs in the Mediterranean Sea. Consequently, the official report of EEA (2014) recommended to automatically associate water quality assessment with regular measurements of water discharges at the same monitoring site.

Algerian estuaries are still less well-known, only a few of them have been explored for water and nutrient inputs (Khélifi-Touhami et al., 2006; Ounissi and Bouchareb, 2013; Ounissi et al., 2014, 2018). Ounissi and Bouchareb (2013) assessed the role of reservoirs in water and nutrient retentions in three coastal catchments (Kebir-Rhumek, Kebir West, Saf-Saf). Other studies investigated the water and nutrient inputs at the Seybouse and the Mafragh estuaries' outlets. Until now, no study has considered the flow and associated nutrient inputs into the estuary and the latter inputs into the adjacent coastal waters. In addition, although silica is indicated as a proxy of freshwater influence and a limiting factor for diatom growth. Studies on Algerian estuaries have rarely monitored silica level and load. Similarly, the dissolved organic N and P forms have also been omitted in most of those studies, despite the importance and the role they play as bioavailable nutrients in N and P cycling in the highly dynamic coastal ecosystems.

To fulfill these crucial gaps, we assessed water discharges and nutrient loads from two Seybouse river gauging stations over a one-year study period (January–December 2012). During this period, a heavy rainfall episode occurred in February 2012 heavily affecting the lower-reach of the river estuary. The main objectives of the present study are (1) to characterize the nutrients (organic and inorganic fractions) and loads of the Seybouse River lower-reach entering its estuarine part, (2) to assess the influence of these nutrients and their molar ratio variations in the estuarine section, and (3) to evaluate the potential influence of the outflow on the coastal eutrophication of Annaba Bay.

2. Materials and methods

2.1. Study area

The Seybouse River (6500 Km^2), located in the north-eastern of Algeria, rises at the Atlas Tellian and runs across about 165 km to reach the Annaba bay. The mean precipitation ranges between 350 mm in the semi-arid upper basin to 650 mm in the humid littoral region (Laborde et al., 2010; Ounissi et al., 2018). Seybouse River discharge is highly variable from nearly null flows in summer to extreme flooding events in autumn-winter, which is typical of the Mediterranean river flow regime. A mean discharge of 14 $m^3 s^{-1}$ was reported by LCHF (1976) and UNEP/MAP (2013). Despite its limited surface water resource, the Seybouse catchment is highly regulated by two large dams (Charef and Bouhamdane) and ten weirs that together retain approximately 400 hm^3. This water is mostly used to supply large irrigated areas and to fulfill the population's drinking-water needs. Supported by such a water storage, important agricultural activities are expanding over the middle and lowermost catchments (cereals, vegetable crops, and fruit trees). UNEP/MAP (2013) reported an irrigated area of 25,000 ha (3–4% of the total catchment area), for the two last decades, which now expands over most of the Seybouse valley. In addition to several agro-food industries located in the middle (Guelma, Bouchegouf) and the lower basin, an array of other industries were set up in the lowermost Seybouse catchment. The areas of Meboudja and Pont Bouchet (Fig. 1;

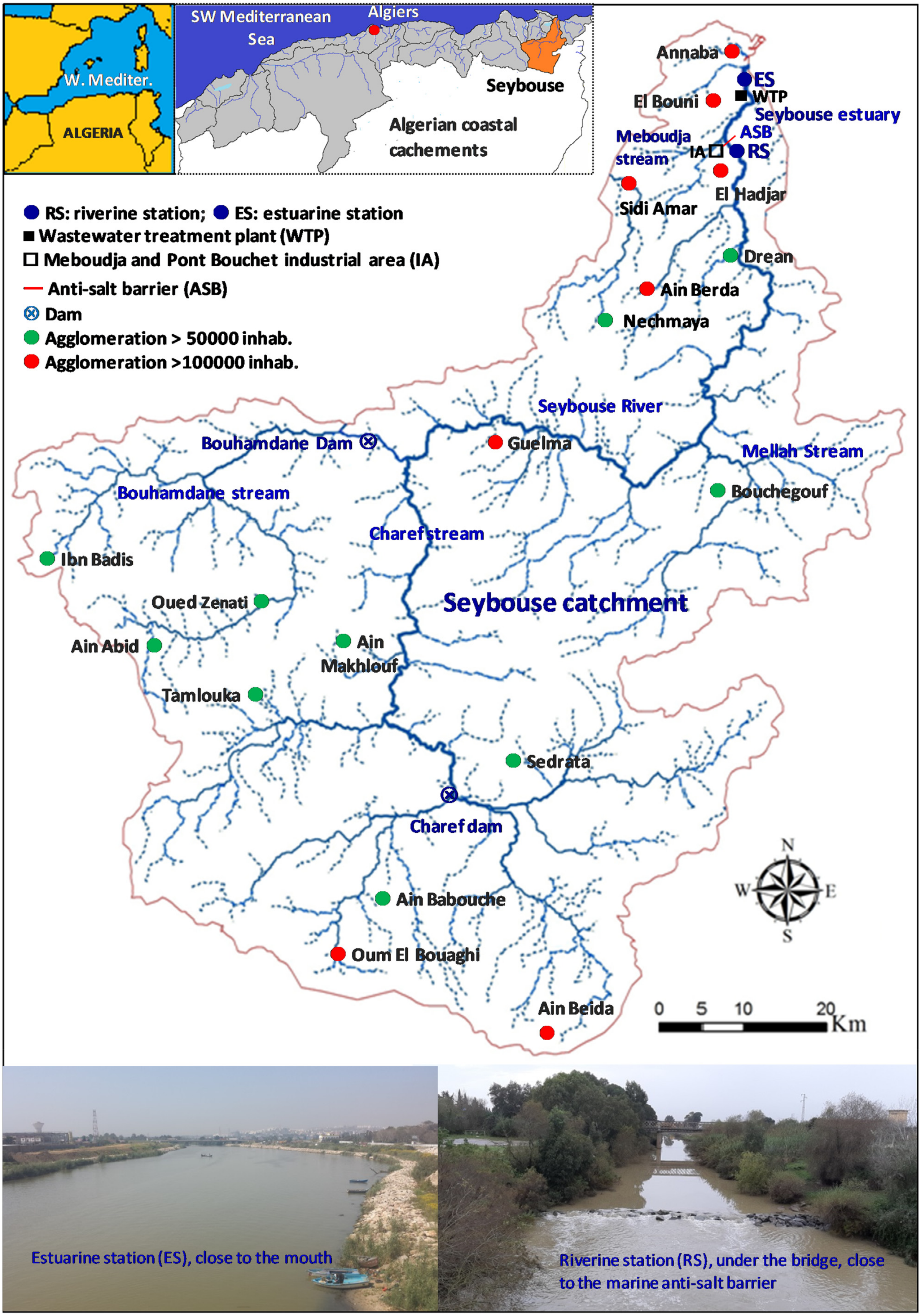

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Fig. 1. Study area showing the sampling stations (RS = Riverine Station; ES = Estuarine Station), the anti-salt barrier (ASB), the industrial areas (IA) and the wastewater treatment plant (WTP) in the lowermost river estuary. The locations of the major cities in the Seybouse catchment are also shown.

Table 1) include large industrial zones (IA) as El-Hadjar complex (metal steel plants), cement factory, agro-food factories, paper and plastics factories (Belabed et al., 2017). The water volume allocated to these industries may reach 45,000 m^3 per day (ABH, 2013). All their sewers are directly discharged (without treatment) into the Meboudja stream, which joins the upper estuarine part at about 7 km from the outlet (Fig. 1, Table 1). The Meboudja stream also exhibited huge household wastes from numerous surrounding villages. Add to this the wastewater treatment plant located at the lowermost estuary (WTP, Fig. 1), near the mouth, which releases over 40,000 m^3 per day (80,000 inhab. Equiv.) of wastewater, frequently without treatment. These are the major sources of heavy and various pollutants, which could be concentrated in the estuarine part, before reaching the outlet of the estuary.

The Seybouse River has a small estuarine part affected by microtidal and a semi-diurnal regime. This estuarine part has been reduced by building an anti-salt barrier at 8 km from its outlet (Fig. 1, Table 1), to prevent salt contamination of the adjacent agricultural lands by the marine saltwater intrusion. Otherwise, the tidal intrusion could reach and gain a large inland part of the Annaba plain because of the weakness of the low of the plain slope (0.1% at 20 km inland). The estuary is a highly stratified system, where surface freshwater flows into the sea, above the deep marine water moving landward, following a semi-diurnal microtidal regime. However, this common basic regime could be entirely changed by high river flow, where the salt wedge can be driven-back up to the coastal river plume. This might last for several days occulting any marine tidal penetration. The tidal regime revertion is still possible if the river flow declines to about 30 m s^{-1}. The advance or retreat of the salt wedge depends mainly on river discharge, which is itself directly linked to weather conditions (precipitation, wind speed, storm surge).

2.2. Sampling and analytical methods

The lower Seybouse River was sampled twice a month in 2012 at its respective riverine (RS) and estuarine stations (ES), as shown in Table 1 and Fig. 1. Water flow and hydrological variables were simultaneously measured at the two stations (Fig. 2a, b). Measurements of temperature (°C) and salinity (practical salinity unit: psu) were performed in situ using a Multi-parameter WTW 1970i. Water sampling for nutrient determination was made on the upper layer surface water as shown in the Fig. 2a and b. The dissolved inorganic nitrogen DIN (ammonium: NH_4; nitrate: NO_3; nitrite: NO_2), dissolved organic nitrogen (DON), phosphate (PO_4) and silicates ($Si(OH)_4$) 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 method of Rodier (1996). Dissolved organic phosphorus (DOP) was obtained by subtracting the dissolved inorganic phosphorus (DIP = PO_4 + P_2O_5) from TDP. The relative precisions are: 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%.

To assess the water discharge ($m^3\ s^{-1}$), current velocity at RS and ES were measured using a CM-2 current meter (Toho Dentan Co., Ltd., Tokyo) and calculated by multiplying the water velocities by the total surface areas (m^2) of both the riverine and estuarine wet sections (e.g. Fig. 2a). Measurements of water velocity were taken at several points along the wet section, this allowed computing the average current velocity (e.g. Fig. 2a). As shown in Fig. 2a, the current velocities were not homogenous both vertically and horizontally in the water layer, they varied slightly for this example (10–20 cm s^{-1}). Although the wet section width and the water depth were among the highest ones of the year (Fig. Supplemental data), the corresponding water flow was only about 12.5 $m^3\ s^{-1}$ because of the low current velocities recorded at this time. This is an exemplified picture of how we estimated the water river flow at a specific sampling date.

Fig. 2b shows the salinity profiles for 12 sampling dates, where the freshwater layer can easily be identified. The salinity threshold selected to define the freshwater from the saline water, in the surface water layer, was < 2 psu. Soils of the Seybouse drainage basin are heavily saline, typical of the North African soils (Aubert, 1976), reaching > 4 g L^{-1} by dry season. This affects and increases the freshwater salinity draining those saline soils.

Estimations of freshwater flow were then calculated using the freshwater layer shown in Fig. 2b (and in the Supplemental figure). This is a method we usually used (Ounissi et al., 2014) in estimating

Table 1
Main characteristics of the sampling riverine and estuarine stations (riverine station: RS; estuarine station: ES).

	Riverine station (RS)	Estuarine station (ES)
Location	36°47′55.87·N - 7° 46′27.60·E	36°51′56.00·N - 7° 46′10.90·E
Altitude	7 m	1 m
Distance to the sea	8 km	100 m
Wet section configuration	Depth 0.5–2 m Width 10–15 m	Depth 1–8 m Width 20–100 m
Specific layout	Close to the anti-salt barrier	Close to an anti-flood channel, at about 100 m from the shoreline
Catchment area	5752 km^2	6740 km^2
Main source of pollution	- Under large agricultural lands runoff -Submitted to direct wastewater inputs from Drean and El-Hadjar cities as well as several other surrounding villages	- The upper estuarine part is heavily impacted by various industrial wastes from Meboudja and Pont Bouchet industrial areas as well as El-Hadjar metal steel factory - The upper estuarine part receives direct wastewater without any treatment from several cities (El Hadjar, El Bouni, Pont Bouchet, Sidi Ammar) and villages - The lowermost estuarine part receives directly a great sewer (40,000 m^3 per day) from the wastewater treatment plant, located near the estuary (150 m), and about 700 m from the estuary's mouth
Main hydrological features	- Typical freshwater with salinity frequently not detectable (near zero) in the wet season. - The station is located before the anti-salt barrier	- Tidal zone with semidiurnal regime and large stratification - The high river flow in wintertime can push the whole estuarine water layer to retreat up to the sea
Sampling date	Jan. 10, 28; Feb. 14, 29; Mar. 14, 25; Apr. 14, 26; May 13, 24; Jun. 03, 20; Jul. 02, 16; Aug. 11, 25; Sep. 03, 21; Oct. 04, 28; Nov. 15, 27; Dec. 14, 29	The same sampling dates of the riverine station

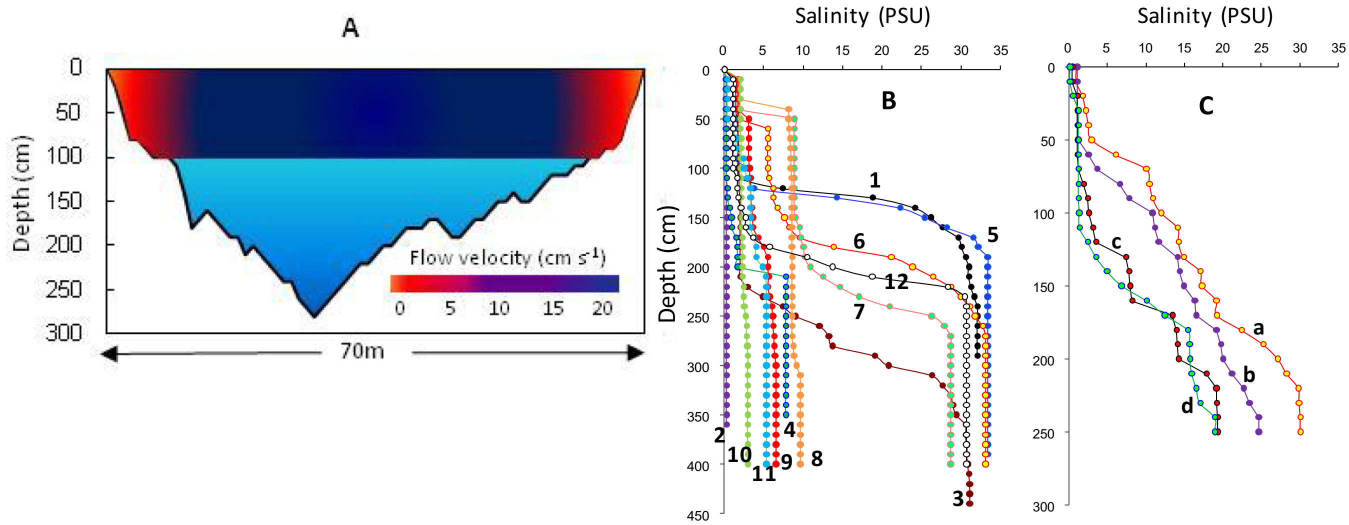

Fig. 2. A: example of 18 January 2012 (= 1 of Fig. 2b) showing the distribution of the surface current velocity measured on the freshwater layer (0–100 cm) and the bathymetric configuration at the Seybouse estuary outlet. B: example of vertical profiles of salinity at the Seybouse estuary's outlet during the sampling period, January–December 2012. 1: 28.01.2012; 2: 29.02.2012; 3: 25.03.2012; 4: 26.04.2012; 5: 24.05.2012; 6: 20.06.2012; 7: 16.07.2012; 8: 25.08.2012; 9: 21.09.2012; 10: 28.10.2012; 11: 27.11.2012; 12: 29.12.2012. a and b allowed determining the freshwater layer and freshwater discharge at the Seybouse outlet. C: an example of the salinity profiles along the Seybouse estuary (10 October 2015), showing changes in the freshwater layer thickness along the estuarine part. a: outlet station (ES); b: 3 km from the outlet; c: 6 km from the outlet; d: 8 km from the outlet (close to the anti-salt barrier).

freshwater flow delivery from a complex estuarine outlet, changing at tidal or even at an hourly scale.

The water flow ($m^3 s^{-1}$) at each station was determined by multiplying width (m) by the depth of the freshwater layer (m) by the current velocity ($m s^{-1}$).

2.3. Water and nutrient fluxes estimation and index of coastal eutrophication potential (ICEP)

Instantaneous nutrient fluxes were calculated by multiplying their respective concentrations per river flow and expressed as kg day^{-1}. The annual flux of nutrients was estimated using the average instantaneous flow method (Preston et al., 1989).

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

where F is the annual flow (tons per year or tyr^{-1}); Ci is the concentration of the nutrients (kg m^{-3}); Qi is the concomitant instantaneous flow ($m^3 d^{-1}$); n is the number of days of the concentration data and K is the conversion factor considering the period of study (365 days) and the unit of estimation.

The index for coastal eutrophication potential (ICEP) is a synthetic indicator proposed by Billen and Garnier (2007) to assess the potential of river systems for coastal eutrophication. The ICEP considers that many coastal eutrophication problems are the consequence of the new production of non-siliceous algae sustained by N and P delivered in excess over dissolved silica, with regard to the requirements for diatom growth. Consequently, the ICEP represents the carbon biomass potentially produced in a coastal water body through new production sustained by the riverine flux of N or P delivered in excess over Si. It is based on the Redfield molar C:N:P:Si ratios (106:16:1:20, Redfield et al., 1963) and according to the nutrient considered, either N-ICEP or P-ICEP can be defined, following relationships (2) or (3), respectively:

$$N - ICEP = [N_{Flx}/(14 \times 16) - Si_{Flx}/(28 \times 20)] \times 106 \times 12 \tag{2}$$

$$P - ICEP = [P_{Flx}/(31 \times 1) - Si_{Flx}/(28 \times 20)] \times 106 \times 12 \tag{3}$$

where P_{Flx}, N_{Flx} and Si_{Flx} are, respectively, the mean specific fluxes of total nitrogen (TN = TDN + particulate N), total P (TP = TDP + particulate P) and dissolved silica (Dsi = $Si(OH)_4$) delivered at the outlet of the river catchment, expressed in kg P km^{-2} day^{-1}, in kg N km^{-2} day^{-1} and in kg Si km^{-2} day^{-1}. As described in the work of Billen and Garnier (2007), the ICEP is expressed in kg C km^{-2} day^{-1}, and by units of catchment area, to allow comparisons between rivers. Positive value of the ICEP indicates an excess of N or P over the requirements for diatom growth, hence a favorable condition for the development of harmful non-siliceous algae. Negative value indicates that silica is present in excess over N and P and thus, less risk of eutrophication.

In addition to computing ICEP by using TN, TP and DSi fluxes, as from the method of Billen and Garnier (2007), we also attempted to compute two additional ICEP options. Because TN and TP fluxes are not always available, they can be replaced by their respective total dissolved forms (TDN and TDP), and used with the Dsi fluxes (to have more homogeneous forms) in the estimation of ICEP. This is the first option. Also, data on total Si (DSi + particulate biogenic silica or BSi), TN and TP fluxes can all be available for a given river outlet, and could better be used for ICEP estimations (Romero et al., 2013). This is the second option, and the third one is that of Billen and Garnier (2007). In the second and third options, as we have only the total dissolved forms of Si, N, P, we added their respective particulate fractions from Ounissi et al. (2018), whose data (54 weekly samples for the relatively dry year of 2014) on the Seybouse estuary outlet included the particulate forms. The mean particulate fractions were: 30% for particulate biogenic silica, 34% for particulate P and 5% for particulate N. We then compared the three ICEP different types: (1) ICEP based on DSi, TDN, TDP; (2) ICEP of Billen and Garnier (2007) and (3) ICEP based on total forms (TSi, TN and TP).

2.4. Statistical analyses

Statistical analyses were performed using Statgraphics Centurion XVIII trial version 18.1.11 (Statpoint Inc.; USA). The data set was tested by one-way ANOVA and expressed as mean ± standard errors to compare the difference between fortnightly samplings of material in the riverine and the estuarine stations with a significance threshold at $P = 0.001$. The relationships between the 15 hydrological parameters measured in 48 samples at each station (upstream and outlet) were also assessed with the correlation coefficient computed using the same

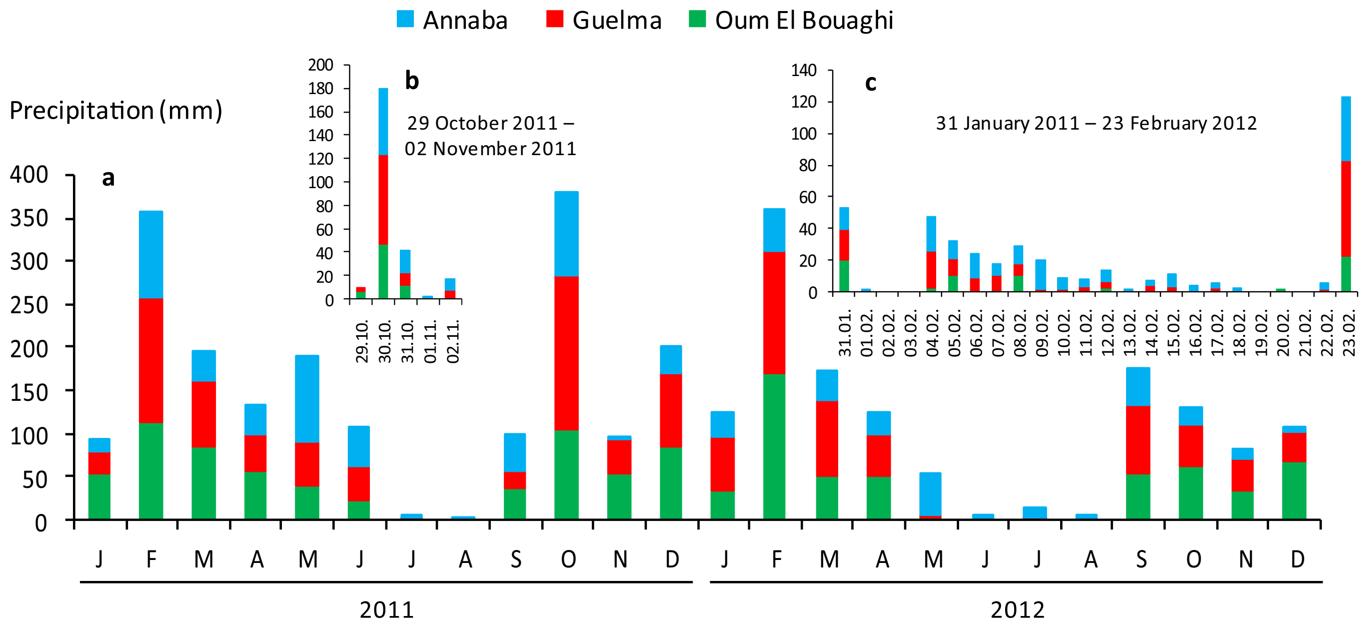

Fig. 3. a: Monthly precipitation height (mm) over the upper (Oum El Bouaghi), middle (Guelma) and lower (Annaba) Seybouse catchments in 2011 and 2012. b: Daily precipitation from 29 October to 2 November 2011. c: Daily precipitation from 31 January to 23 February 2012. b and c would have triggered together the flooding event of late February 2012. Precipitation data are from the National Office of Meteorology (ONM).

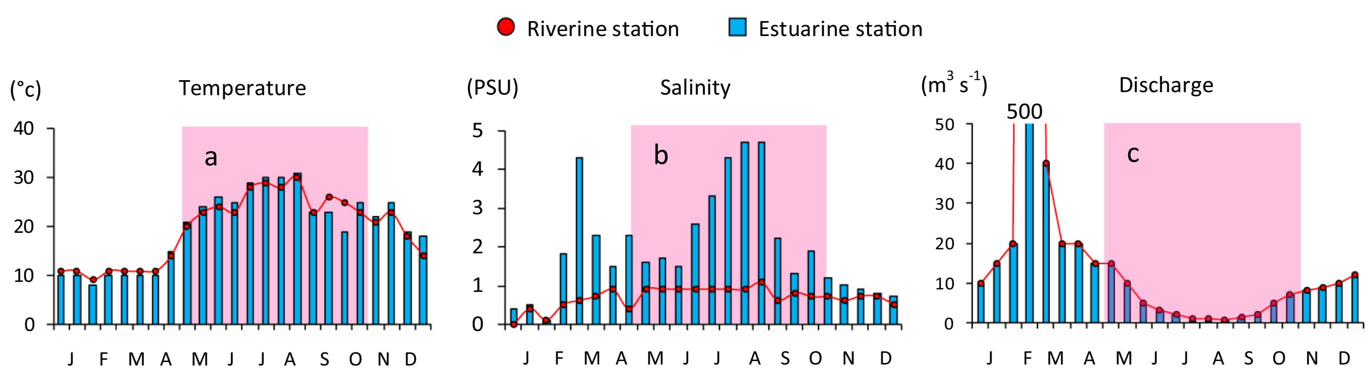

Fig. 4. Seasonal variations in hydrological parameters at the riverine and estuarine stations of the Seybouse River estuary during January–December 2012. The pink color area represents the dry season. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

software.

3. Results

3.1. Precipitation and flooding event

Precipitation data over the upper, middle and lower Seybouse catchment in 2011 and 2012 are shown in Fig. 3a. The year 2011 was relatively wet in contrast to the year 2012 which was dry over the whole Seybouse catchment. From the total yearly amount, the basin had received over a third (Oum El Bouaghi) to about half (Annaba, Guelma) the precipitation yield during September–December 2011. The middle catchment (Guelma) during that year, had received more rainfall than the usually wetted lower catchment (Annaba) and the usually dry region of Oum El Bouaghi (Fig. 3b). The year 2012 was relatively dry, and most precipitation occurred between January and April. This wet period contributed 344 mm (63%), 305 mm (57%) and 135 mm (48%) of the total annual precipitation, in Guelma, Annaba and Oum El Bouaghi, respectively. Within this wet period, an exceptionally heavy rainfall event occurred on 23 February over the whole basin with a maximum daily precipitation of 61 mm in Guelma, 40 mm in Annaba and 22 mm in Oum El Bouaghi. The heavy precipitation occurring in early October 2011 (Fig. 3b), followed by continuous and abundant precipitation between 4 and 15 February (Fig. 3c), contributed to increasing soil saturation. This had later coincided with the 23 February 2012 heavy rainfall and triggering a strong river flooding event. Because flash floods remain unpredictable and devastating in the developing countries, the flood event of late February 2012, was unfortunately not sampled right from the start. The freshwater flow measurements were taken only 4 days after the flood began because the sampling stations were not accessible. Runoff exceeding 1600 $m^3 s^{-1}$ could have occurred due to the high soil moisture and runoff coefficient of the catchment (30–35%). This heavy rainfall episode has also increased groundwater flows, particularly in the middle and lower catchment, which are not regulated.

3.2. Seasonal variations of hydrological parameters at the riverine and the estuarine stations

The hydrological parameters recorded during January–December 2012 are shown in Fig. 4. During the study period water temperature fluctuated between 13.9 °C in January and 25.5 °C in August (Fig. 4a). The general trend of temperature is comparable for both sampling stations but the annual average value at the outlet station was slightly

Table 2
Mean seasonal (± standard deviation) values of hydrological parameters for the Seybouse estuary in 2012.

Period	Freshwater flow at the outlet ($m^3 s^{-1}$)	Depth of the halocline interface (m)	Volume of freshwater within the estuary ($\times 10^3 m^3$)	Freshwater Residence time at the estuarine part (h)[c]	Volume of freshwater delivered to the sea ($\times 10^6 m^3$)
Winter	94.5 ± 198.7	1.73 ± 1.1	277 ± 176	3 ± 2.2	735 ± 1545 (77%)[a]
Spring	20 ± 10.5	1.57 ± 0.7	257 ± 107	3.5 ± 1.1	156 ± 81.6 (16%)
Summer	2.1 ± 1.7	0.30 ± 0.1	48 ± 16	8.4 ± 3.7	16.2 ± 13.1 (2%)
Autumn	5.4 ± 3.1	0.50 ± 0.2	80 ± 32	5 ± 2.3	42.2 ± 24.4 (5%)
Annual	30.5 ± 43.4	1 ± 0.7	665 ± 117	5 ± 2.4	949[b]

[a] 88% of the winter freshwater delivery was brought during the flood event of late February 2012.
[b] 68% of the annual freshwater delivery was brought during the flood event of late February 2012.
[c] The residence time (volume of the estuary/discharge) was estimated following Rueda et al. (2006).

higher because of the influence of additional warm water inputs from both the wastewater treatment disposal and the influence of waters from Meboudja stream. The surface water salinity slightly varied throughout the seasons (0–1.1) at the riverine station but markedly increased (up to 4 psu from lowest records) at the estuary. By wet season, both stations showed typical freshwater salinity and varied in a small range (Fig. 4b). At the estuarine station, the halocline depth decreased to 0.3 m in summer and 0.5 m in autumn, but was more important in winter and spring (1.73 m and 1.57 m respectively, Table 2). The freshwater volume within the estuary depends on the depth of the halocline interface (Table 2). In winter and spring, the freshwater volume accounted for 80.5% of the annual amount, while it represented just 7.3% and 12.2% in summer and autumn, respectively (Table 2).

Freshwater discharges varied greatly throughout the seasons and followed closely the seasonal precipitation distribution (Fig. 4c) with high and significant correlation ($r = 0.82$, $p < 0.01$). Consequently, the maximum water discharge occurred from November to April and the minimum one took place during the dry period, extending from May to October. In summer very low flows, not exceeding on average 2.1 $m^3 s^{-1}$, were observed at the outlet, and in August the estuary was nearly disconnected from the sea (Fig. 4c, Table 2). By dry season and due to the lack of rain, direct water abstraction for irrigation needs and the very low tide range ($\approx$20 cm), the estuarine water flow diminished. This resulted in increasing the water residence time to 5–8.4 h (Table 2). In the wet season, the water flow substantially increased and peaked to 500 $m^3 s^{-1}$ in late February producing a large flood event (Fig. 4c). This resulted in large freshwater delivery into the Annaba bay (949 $10^6 m^3$). The flood of February 2012 contributed 68% towards the annual water volume delivery (Table 2). A large fraction of annual freshwater delivery, as high as 77%, was brought in winter, of which 88% was due to the flood event of late February 2012. Together, summer and autumn freshwater supply only amounted to 7% of the yearly volume.

3.3. Seasonal variations in nutrients level at the riverine and the estuarine stations

As shown in Fig. 5, nutrient concentrations at both stations presented intense seasonal variation. Such a large seasonal variability was also confirmed by the one-way ANOVA (Table 3), with high concentrations during the dry period. The total dissolved nitrogen (TDN) levels displayed a clear seasonal pattern with strong amounts during the dry period, reaching on average 132 µmol L^{-1} at the riverine station and 142 µmol L^{-1} at the estuarine station (Fig. 5a). In the wet period, TDN levels decreased by about one third those of the dry season. TDN annual average levels were not much different in both stations, with slightly high amounts at the estuarine station (average 120 µmol L^{-1}) and 109 µmol L^{-1} at the riverine station. The major component of TDN was ammonium (NH_4), which constituted an average of 57% at the riverine station and 60% at the estuarine station. In the dry season, NH_4 fraction increased to 67% in both stations. Seybouse waters were strongly charged with NH_4 especially during the dry season, with mean levels of 89 µmol L^{-1} at the riverine station and 95 µmol L^{-1} at the estuarine station. There is a high and significant negative correlation between NH_4-river flow ($r = -0.30$; $p < 0.05$). By dry season, NH_4 amounts decreased by > 50% that of the wet period values. Also, NH_4 had an inverted seasonal cycle compared to that of nitrates (NO_3), evidenced by a high and significant negative correlation NO_3-NH_4 ($r = -0.53$; $p < 0.001$). The second important component of TDN pool was NO_3, accounting for an important fraction in the wet period in both riverine (45%) and estuarine stations (37%). NO_3 levels clearly followed a seasonal cycle, with high and comparable values (37–39 µmol L^{-1}) in the wet period at both stations (Fig. 5f). In the dry season, NO_3 amounts decreased by about 30% of the wet season values, while they were sensibly comparable in the two stations (Fig. 5f). Although it represented a small portion (4–7%) of TDN, nitrite (NO_2) was abundant in the Seybouse with an average value of 5.2 µmol L^{-1} at the riverine station and 7.4 µmol L^{-1} at the estuarine station (Fig. 3e). As for NH_4, NO_2 levels were always higher at the outlet water, particularly during the dry season.

The dissolved organic nitrogen (DON) contributed only 8% to the TDN amounts and varied over a small range through the seasons in both riverine (7.8–10.3 µmol L^{-1}) and estuarine (9.3–11 µmol L^{-1}) stations. As for the reduced nitrogen form NH_4, the organic reduced form DON increased slightly at the estuarine station. Although the DON did not show a clear seasonal pattern (Fig. 5c), it was found to have a good correlation with NH_4 ($r = 0.3$; $p < 0.05$). Dissolved inorganic nitrogen (DIN = NO_3 + NO_2 + NH_4) largely dominated the TDN amount, amounting to 92% at all stations. DIN was greatly dominated by NH_4 and follows then the same seasonal cycle of NH_4 (Fig. 5b). This is largely evidenced by the strong DIN-NH_4 correlation ($r = 0.94$; $p = 0$). The total dissolved phosphorus (TDP) displayed high values during the dry period, reaching on average 16.7 µmol L^{-1} for the riverine station and 19 µmol L^{-1} for the estuarine station. This represented the double amounts of the wet season (Fig. 5a). The sole little difference noticed in TDN levels was a slight increase of 15% at the estuarine station (15.2 µmol L^{-1}) compared to the riverine one (13.1 µmol L^{-1}). TDP had a similar seasonal pattern to TDN with a good and significant correlation coefficient ($r = 0.49$; $p < 0.001$).

The phosphate (PO_4) levels showed an apparent seasonal pattern (Fig. 5j) with high amounts in the dry season (7.7–8.2 µmol L^{-1}), which represented an increase of 37–45% the values of the wet period for riverine and estuarine stations, respectively. The annual PO_4 mean, which represented a large fraction of TDP (44–46%), was comparably high at both stations (6–6.7 µmol L^{-1}). Considered as proxies of anthropogenic influence, PO_4 and NH_4 showed high amounts especially

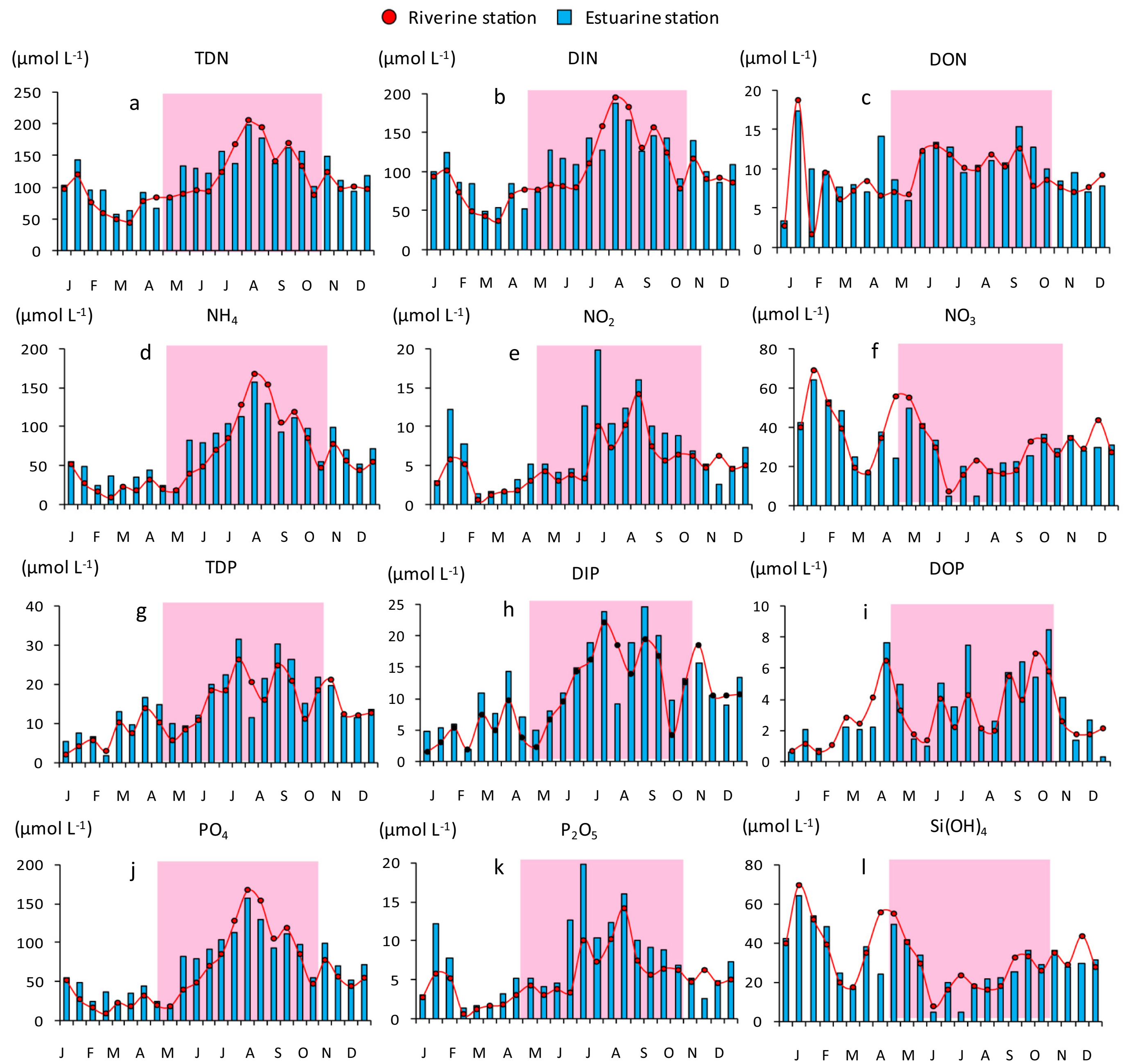

Fig. 5. Seasonal variations in nutrient levels at the riverine and estuarine stations of the Seybouse River estuary during January–December 2012. The pink color area represents the dry season. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

during the dry period as well as a largely significant correlation (r = 0.67, p = 0). Similarly to the PO_4 pattern, Seybouse waters showed high polyphosphate (P_2O_5) mean levels (4.2–5.1 µmol L^{-1}) at both riverine and estuarine stations (Fig. 5k), At seasonal scale, there was an important increase of P_2O_5 amount by about 50% during the dry season. Whatever the season, P_2O_5 still represented a substantial amount, up to and one third of the TDP total load. The dissolved organic phosphorus (DOP) represented a considerable proportion of TDP, varying from 20 to 24%. It showed similar seasonal fluctuation, with increased amounts in the dry season (Fig. 5i). Average annual levels for the two stations were elevated as high as 2.94 µmol L^{-1} at the riverine station and 3.35 µmol L^{-1} at the estuarine station. Similarly to all the nutrients (except for NO3), DOP levels slightly increased from the riverine to the estuarine station. Dissolved inorganic phosphorus (DIP = PO_4 + P_2O_5) levels fluctuated widely (Fig. 5h), reaching high amounts in the dry period (13–14.8 µmol L^{-1} on average). Mean values for the wet period dropped down by about 40–45% relative to dry season. A negative correlation was found between DIP and water flow (r = −0.33; $p < 0.05$). DIP annual mean (10.2–11.8 µmol L^{-1}) in the Seybouse waters accounted for 76–80% of the TDP amount.

Silicates $Si(OH)_4$ amounts followed the same seasonal cycle of NO_3 and river flow. A strong and highly significant correlation was found between river flow and $Si(OH)_4$ (r = 0.74, p = 0), as well as another good one between $Si(OH)_4$-NO_3 (r = 0.35, $p < 0.05$). Levels of the wet season (120–131 µmol L^{-1}) surpass those of the dry season by a factor of 1.7 for the two stations (Fig. 5l). Because $Si(OH)_4$ is mainly of natural origin (from rock weathering), it displayed a clear inverse seasonal pattern to almost all of the other nutrients that could be of anthropogenic origin (e.g. NH_4, PO_4). Seybouse waters were not poor in Si $(OH)_4$ for this one-year study, having moderate levels

Table 3
One-way ANOVA results (F: Fisher test) showing variation factors between stations (RS and ES) and seasons (dry or wet) and variables (flow; salinity and nutrient levels) from $n = 24$ fortnightly samples in 2012.

	Station	Season
	F	F
Flow ($m^3\ s^{-1}$)	0 ns	3.48 ns
Sal (psu)	21.02***	5.64*
NH_4 (µmol L^{-1})	0.63 ns	27.29***
NO_2 (µmol L^{-1})	3.28*	17.5***
NO_3 (µmol L^{-1})	0.12 ns	8.56**
DIN (µmol L^{-1})	0.83 ns	20.6***
DON (µmol L^{-1})	1.43 ns	5.37*
TDN (µmol L^{-1})	1.71 ns	17.17***
PO_4 (µmol L^{-1})	0.37 ns	9.54**
P_2O_5 (µmol L^{-1})	1.6 ns	16.11***
DIP (µmol L^{-1})	0.84 ns	13.6***
DOP (µmol L^{-1})	0.41 ns	10.2**
TDP (µmol L^{-1})	0.95 ns	18.2***
$Si(OH)_4$ (µmol L^{-1})	0.45 ns	31.03***

* significant at the 0.05 level
** significant at the 0.01 level
*** significant at the 0.001 level

(96–104 µmol L^{-1}), where most of samples surpasses 100 µmol L^{-1}.

The Redfield molar ratios ($Si(OH)_4$:DIN:PO_4; herein referred to as Si:N:P) displayed large variations and deviated from the balanced value in both stations (Fig. 6). N:P ratios were more unbalanced during the wet season, reaching on average 27 and 39 at the estuarine and riverine stations, respectively (Fig. 6a). Although the mean N:P ratio did not greatly deviate from the balanced value, only one-half of the samples had nearly balanced values (10 < N:P < 20). Also, 33% of samples displayed elevated values (N:P > 20), resulting in high DIN over PO_4 inputs. However, in 16% of the samples N:P was < 10, indicating high dominance of PO_4 over DIN inputs (Fig. 6a). As shown in Fig. 6b, Si:P had a similar pattern of N:P, with high values (44 and 74 in estuarine and riverine stations, respectively) recorded mainly in the wet season. Although the Si:N mean values appeared to be balanced during the study period (1.26 at RS and 1.16 at ES), they frequently (54%) deviated from the standard Redfield value (Si:N = 1), especially in the dry period. Unlike almost all dry season samples with Si:N < 1 (mean = 0.6) collected at both stations, most wet season samples showed balanced values, Si:N > 1 (Fig. 6c).

3.4. Nutrient loads and ICEP for the riverine and the estuarine lower reaches

Annual along with seasonal loads and yields of various nutrients are shown in Table 4. The Seybouse River introduced 901 t yr^{-1} of TDN into the estuary, of which 57.5%, 26.6%, 13.5% were in the form of N-NO_3, N-NH_4, and DON, respectively (Table 4). Most of these loads were delivered during the wet season, contributed 88.8% (800 t yr^{-1}) of the whole amount. The wet season is characterized by high N-NO_3 loads from the lower Seybouse River, where 60.6% of TDN inputs were in the form of N-NO_3. More importantly, most TDN loads were caused by the flood event of late February, accounting for 60% of the annual load. From all TDN components, N-NO_3 and DON were mainly supplied by the flood event, contributing to 70.2% and 72.8% to the annual load, respectively (Table 4). In addition, the high Seybouse River discharge in 2012, resulted in significant yields of TDN components (Table 4), particularly N-NO_3, which was released at a rate of 90 t km^{-2} yr^{-1}. The Seybouse River brought to the estuary significant masses of TDP, in particular during the wet period, where it contributed 83.6% to the yearly load, corresponding to 132 t. The flood event transported more P_2O_5 and DOP than PO_4, while the annual TDP load was nearly equally shared between the different components (P-PO_4: 33.8%; DOP: 30%; P-P_2O_5: 36.2%). Similarly, the annual yields of TDP components were elevated and comparable (8–10 t P km^{-2} yr^{-1}), as clearly shown in Table 4. The Seybouse River transported large Si-$Si(OH)_4$ amounts (5112 t yr^{-1}), 96.8% of which was delivered during the wet period (889 t km^{-2} yr^{-1}). The contribution of the flood event in Si-$Si(OH)_4$ loads was remarkably dominant (81.9%), unlike the P-PO_4 and N-NH_4 commonly known as proxies of anthropogenic influences.

When reaching the estuarine part, the riverine waters were overloaded with important additional inputs of N-NH_4, N-NO_2, and P-PO_4, that could have mainly originated from the Meboudja stream and the wastewater treatment plant. The relative budget calculations presented in Table 4 indicated an increase of up to 123.5% in N-NH_4, 66.3% in N-NO_2 and 46.6% in P-PO_4 and only a small supply occurred of NO_3, DON, and Si-$Si(OH)_4$. However, about half of the incoming DOP load dissipated at the estuary's outlet as well as a small fraction of P_2O_5. The flood event was more effective at the estuarine part, and its contribution to the annual load increased relative to that of the river part. The flood enriched the estuarine part, mostly in N-NH_4 and P-PO_4, which are mainly supplied through the household wastes. The flood at the riverine part, by contrast, was rather characterized by nutrients of natural origin ($Si(OH)_4$, NO_3). This flood event exported large nutrient amounts into the adjacent coast. Without it not only all estuarine material yields could be greatly reduced, but the functioning of the whole estuary and its adjacent coast could also be deeply changed.

Fig. 7 shows the seasonal variations of the indicator of coastal eutrophication potential (ICEP). Generally, ICEP positive values occurred throughout the seasons, except during and after a few weeks the flood event of late February 2012. In the period of high river flow, $Si(OH)_4$ was delivered in excess over P and N, implying that there is less risk of eutrophication potential for Annaba coastal waters (Figs. 4c and 7). The ICEP positive values occurred mostly during the low flow period, when nutrient inputs from anthropogenic origin, namely PO_4 and NH_4 were dominant over the $Si(OH)_4$. The period with ICEP positive values

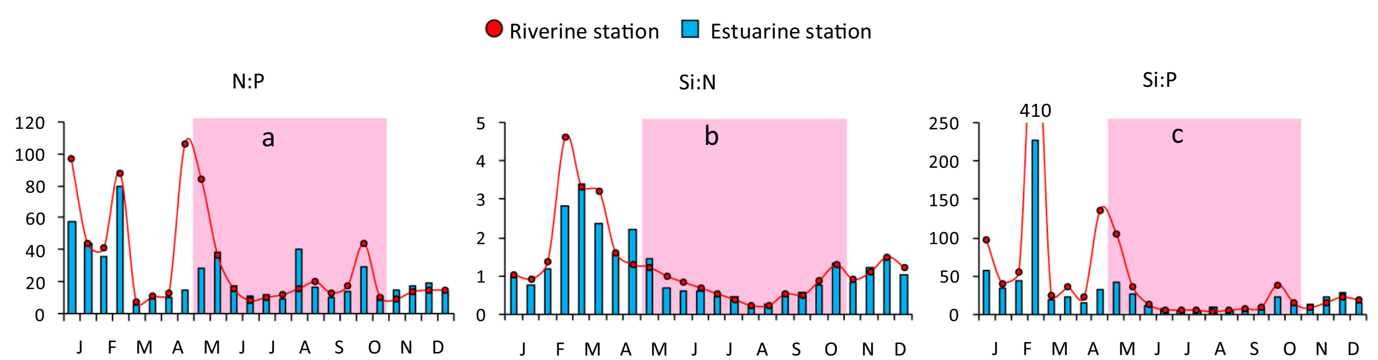

Fig. 6. N:P, Si:N and Si:P molar ratios at the riverine and at the estuarine stations of the Seybouse River estuary during January–December 2012. The pink color areas represent the dry season. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4
Annual and seasonal (dry and wet) nutrient loads and yields from the riverine and estuarine lower parts of the Seybouse River estuary in 2012. The contribution of the flood event of late February is also given. A comparison of different nutrient loads between river inputs into the estuary and the estuary inputs into the Annaba Bay is computed as absolute budget.

	Annual ($t\ yr^{-1}$)		Dry (t)		Dry (%)		Wet (t)		Wet (%)		Flood (t)		Flood (%)		Yield ($kg\ km^2\ yr^{-1}$)		Budget[a] (t)
	RS	ES	RS	ES	RS	ES	RS	ES	RS	ES	RS	ES	RS	ES	RS[b]	ES	
$N\text{-}NH_4$	240	535	51.6	65.7	21.5	12.3	187.9	469.8	78.5	87.7	83.5	332.3	34.8	62.1	41.6	82.8	296
$N\text{-}NO_2$	21	35	4.9	6.9	23.5	19.8	16.1	28.1	76.5	80.2	5.2	13.1	24.9	37.5	3.7	5.4	13.9
$N\text{-}NO_3$	518	593	35.5	34.9	6.9	5.9	482.8	558	93.1	94.1	363.9	445.3	70.2	75.1	90	91.6	74.6
DIN	779	1163	92.1	107.5	11.8	9.2	686.8	1056	88.2	90.8	452.6	790.6	58.1	68	135.4	179.8	385
DON	122	129	8.6	9.6	7.1	7.5	113.1	119.6	92.9	92.5	88.6	89.4	72.8	69.1	21.2	20	7.6
TDN	901	1293	100.7	117.1	11.2	9.1	800	1176	88.8	90.9	541.3	880	60.1	68.1	156.6	199.8	392
$P\text{-}PO_4$	53	78	9.8	12.2	18.5	15.6	43.4	65.9	81.5	84.4	11.3	21.8	21.2	28	9.3	12.1	24.8
$P\text{-}P_2O_5$	57	50	8.2	10.3	14.4	20.6	48.7	39.8	85.6	79.4	28.5	14.7	50.1	29.3	9.9	7.7	−6.8
DIP	110	128	18.1	22.5	16.4	17.6	92.1	105.7	83.6	82.4	39.8	36.5	36.2	28.5	19.1	19.8	18
DOP	47	27	7.7	9.6	16.3	35.7	39.5	17.2	83.7	64.3	21	0.3	44.5	1.1	8.2	4.1	−20.4
TDP	157	155	25.7	32.1	16.4	20.7	132	122.9	83.6	79.3	60.8	36.8	38.6	23.8	27.4	23.9	−2.4
$Si\text{-}Si(OH)_4$	5112	5516	165.5	181.6	3.2	3.3	4947	5334	96.8	96.7	4187	4489	81.9	81.4	889	852.5	403

[a] (ES - RS) for a given nutrient.
[b] the watershed surface up to the RS = the watershed surface of the Seybouse (up to the ES) - the sub-watershed surface of the Meboudja stream (see Table 1).

extended over about 10 months, under which the Annaba Bay could exhibit high risks of eutrophication potential (Fig. 7). It was found that whatever the nutrient forms, upon which the ICEP was computed, all ICEP option values showed the same pattern. However, ICEP values issued from total N (TN), total P (TP) and Dsi or $Si(OH)_4$ were always superior, followed by ICEP computed with total nutrient fluxes (Fig. 7). The lowest values were found with ICEP computed from dissolved forms only (TDN, TDP, and Dsi), but still rather comparable to the ICEP computed from total forms (TSi, TN, TP). Intermediate values were obtained when taking into account the total of the nutrients flux. Overall, our findings indicate that the ICEP could also be computed from the fluxes of the total dissolved nutrient forms, and provides the same pattern of the classical ICEP of Billen and Garnier (2007). This could help using the ICEP for a large number of World Rivers having data only on DSi, TDN and TDP fluxes.

4. Discussion

The year 2012 was relatively dry but had witnessed a heavy rainfall that triggered a strong river flooding, late February, and transported large freshwater discharge ($715 \times 10^6\ m^3$) to the Annaba Bay. This freshwater volume represented 68% of the annual discharge of 2012 and approximately 2-fold the mean multi-annual discharge (UNEP/MAP, 2013; LCHF, 1976). It is also approximately 4-fold the annual freshwater inputs of the severe dry year of 2010 (Ounissi et al., 2016).

Table 5 shows strong inter-annual discharge variability, ranging from $189 \times 10^6\ m^3$ in 2008 to $1170 \times 10^6\ m^3$ in 2009. In addition to the Seybouse water inputs, Annaba bay also received important freshwater flows from the Mafragh catchment, which usually represented 1.5-fold the Seybouse ones (Table 5). Seybouse and many other Algerian adjacent coastal catchments have relatively important freshwater discharges and should not be neglected in the Mediterranean freshwater budget. For example, the 5 rivers presented in Table 5 can collectively provide > 4 km^3 per year. Wang and Polcher (2019) found more freshwater flows into the Mediterranean (40–60%) than previous estimates and hypothesized that a large number of unmonitored coastal rivers were neglected and were a subject to such underestimation of Mediterranean freshwater flows.

The large water amounts delivered from Seybouse River in 2012 have brought significant nutrient masses into the Annaba bay. The Seybouse waters were heavily charged with $N\text{-}NH_4$ (71.7 $\mu mol\ L^{-1}$) in particular, yielding 83 $kg\ N\ km^{-2}\ yr^{-1}$ and $N\text{-}NO_3$ (92 $kg\ N\ km^{-2}\ yr^{-1}$, Table 5). Most of these loads were provided during the flood event of late February, accounting for 62% of $N\text{-}NH_4$ and 75% of $N\text{-}NO_3$ of the annual loads. As clearly shown in Table 5, the Seybouse catchment had the highest levels and yields of $N\text{-}NH_4$, compared to the Mediterranean rivers (e.g., Ludwig et al., 2009; Cozzi et al., 2018), while it had the lowest levels and yields of $N\text{-}NO_3$. However, in most Mediterranean coastal catchments, $N\text{-}NH_4$ fluxes are usually higher than 100–200 $kg\ N\ km^{-2}\ yr^{-1}$ or even more (UNEP/MAP,

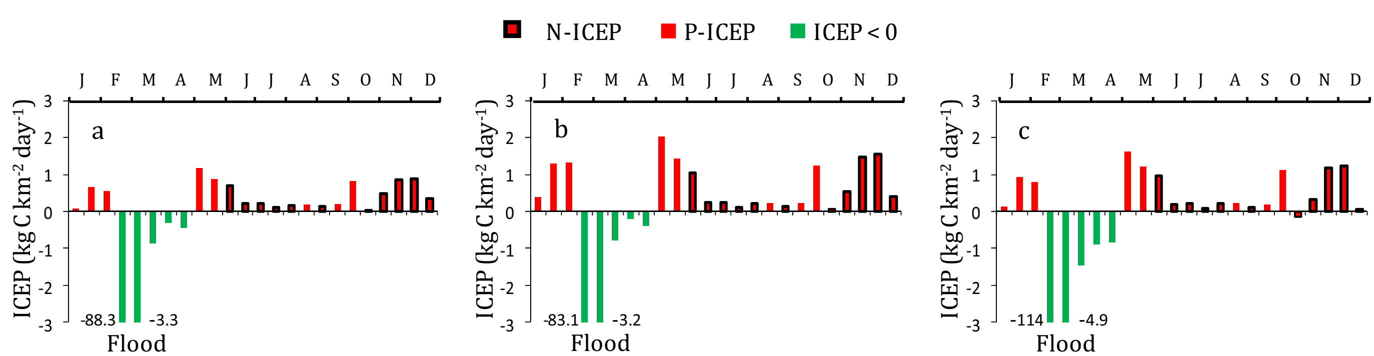

Fig. 7. Seasonal variations of the index of coastal eutrophication potential (ICEP) at the Seybouse estuary's outlet during the study period, January–December 2012.a: ICEP computed from TDN, TDP and Dsi fluxes; b: ICEP of Billen and Garnier (2007); c: ICEP computed from TSi, TN and TP fluxes. N-ICEP and P-ICEP are also shown for each graphic.

Table 5
Nutrient levels (μmol L^{-1}) and yields (between brackets: kg km^{-2} yr^{-1}) of some selected Algerian and other Mediterranean coastal rivers. N:P and Si:N molar ratios are also given. Area: River basin (× 10^3 km^2); Q: Average annual water discharge (× 10^6 m^3).

	Area	Period	Q	NH_4	NO_3	DIN	DON	PO_4***	DOP	$Si(OH)_4$	N:P	Si:N	Reference
Algerian rivers													
KebirRhumel	8.11	2010/2011	1000	14 (12)	17 (17)	33 (31)	21 (13)	2 (6)	12 (14)	65 (111)	51	3.7	Ounissi and Bouchareb, 2013
Kebirwest	1.90	2010/2011	766	9 (85)	23 (45)	39 (222)	18 (112)	4 (58)	10 (65)	77 (1117)	20	4	Ounissi and Bouchareb, 2013
Safsaf	1.16	2010/2011	820	26 (136)	12 (38)	44 (296)	15 (42)	6 (48)	4 (67)	96 (2694)	13	5	Ounissi and Bouchareb, 2013
Mafragh	3.20	2007	1325	7.4 (73)	15.4 (71)	24.2 (154)		1.8 (13)		51.4 (763)	13.4	2.12	Ounissi et al., 2014
		2008	315	6.38 (8)	11.3 (22)	19.9 (34)		1.8 (3)		52.3 (160)	10.8	2.63	Ounissi et al., 2014
		2009	1103	10.6 (50)	17.9 (65)	33.6 (144)		2.5 (28)		55.5 (706)	13.4	1.65	Ounissi et al., 2014
		2010	915	6.7 (27)	16.3 (30)	26.3 (105)	19.2 (78)	1.7 (15)		50.6 (405)	15.5	1.92	Ounissi et al., 2016
		2014	470	8.2 (20.8)	23.4 (78)	34 (104)	8.6 (6.8)	2.1 (10)	2.9 (6.9)	41.1 (257)	15.9	1.21	Ounissi et al., 2018
Seybouse	6.47	2007		228	15.7	258		6.3		57.1	41.1	0.22	Ounissi et al., 2014
		2008	189	151 (57)	36.6 (16)	195 (77)	16[a] (6)[a]	6.5 (2)	4[a] (3)[a]	57.4 (55)	30.1	0.29	Ounissi et al., 2014
		2009	1170	179 (543)	33.9 (79)	224 (640)	30[a] (58)[a]	5 (15)	5.1[a] (19)[a]	104 (752)	44.8	0.46	Ounissi et al., 2014
		2010	630	68 (93)	31.4 (43)	109 (164)	18 (25)	5.1 (15)		66.1 (180)	21.4	0.61	Ounissi et al., 2016
		2014	370	34.9 (18.6)	32.4 (33.4)	75.2 (58.6)	14.1 (4.6)	4.5 (6.3)	4.2 (3.4)	50.3 (129.4)	16.7	0.67	Ounissi et al., 2018
		2012	949	71.7 (83.0)	31 (92.0)	110 (180)	10.2 (20)	6.7 (12.1)	3.4 (4.1)	103.8 (853)	23 0.5	1.16	This study
Mediterraneanrivers													
Medjerda, Tunisia	24.00	1993/1999	1175		143 (98)								UNEP/MAP, 2013
Moulouya, Morocco	55.00	2000/2010	1375	68 (22.8)	128 (43)			25.8 (6.4)					UNEP/MAP, 2013
Gediz, Turkey	16.80	2000/2010	1478	125 (190)	63.6 (96.4)	201 (304)		10.6 (36.8)					UNEP/MAP, 2013
Seyhan, Turkey	20.45	2000/2010	8010	17 (94)	101 (556)	136 (744)		5.9 (74.4)			23		UNEP/MAP, 2013
Ceyhan, Turkey	22.00	2000/2010	7180	20.7 (94.7)	117 (536)	142 (650)		2.2 (22.9)			64.5		UNEP/MAP, 2013
Axios, Greece	23.75	2000/2010	3087	10 (18.4)	140 (258)	158 (291)		17 (71)		(1972)[b]	9.3		UNEP/MAP, 2013
Evros, Greece	53.00	2000/2010	7000	40 (73.9)	83 (153)	134 (247)	21[c] (38.7)**	15 (63.3)	0.94[c] (4)**		8.9		UNEP/MAP, 2013
Aliakmon, Greece	8.88	2000/2010	2700	10.7 (45.6)	76.4 (325)	89.3 (380)		4.1 (39.5)		(2638)[b]	21.8		UNEP/MAP, 2013
Gallikos, Greece	1.05	2000/2010	1246	27.8	140	169 (850)[b]	63	3.1 (37)[b]		(2550)[b]	54.5		UNEP/MAP, 2013
Pinios, Greece	10.74	2000/2010	2550	54.3 (180)	149 (496)	211 (700)		21.9 (166)		(3489)[b]	9.6		UNEP/MAP, 2013
Krka, Croatia	2.29	2000/2010	1740	1.43 (11.8)	20.7 (201)	22.1 (215)	9.3 (90.3)	0.31 (5.46)			71.3		UNEP/MAP, 2013
Neretva, Croatia	8.70	2000/2010	8740	1.4 (24.3)	44.3 (623)	45.7 (643)	17.1 (241)	0.31 (5.3)			18.4		UNEP/MAP, 2013
Ebro, Spain	84.23	1914/2012	10,344	2.8 (4.7)	165 (275)	171 (285)	21.4[d] (35.6)*	2.3 (8)	00[d] (00)*	130 (434)	72	0.7	Cozzi et al., 2018
		2000/2010	13,660	5 (7.29)	175 (255)	181 (266)	14.3 (20.7)	1.9 (6.3)			95		UNEP/MAP, 2013
		1999/2000	5992	5.6 (4.4)	147 (146)	154 (153)		1.5 (2)		66 (140)	103	0.43	Falco et al., 2010
Ter, Spain	3.01	2000/2010	330	16.4 (24.3)	205 (314)	229 (350)	20.7 (41.9)	4.4 (15.4)			52		UNEP/MAP, 2013
Rhône, France	95.59	1920/2012	52,507	3.3 (15.4)	97 (451)	102 (480)		1.5 (15.5)		64 (596)	73	0.6	Cozzi et al., 2018
		2000/2010	53,520	5 (38.4)	106 (816)	112 (866)	10.2[d] (78.5)**	1.6 (27.4)	0.7[d] (11.9)*		70		UNEP/MAP, 2013
Têt, France	1.34	2000/2010	330	121 (383)	104 (331)	238 (756)	57.9 (184)	4.7 (34)					UNEP/MAP, 2013
Argens, France	2.53	2000/2010	580	4.3 (11.3)	80.7 (213)	87.1 (230)	33.6 (88.7)	1.9 (11.3)			46		UNEP/MAP, 2013
Herault, France	2.55	2000/2010	1330	5 (23.3)	40.7 (221)	45.7 (248)		0.63 (7.76)			73		UNEP/MAP, 2013
Tech, France	0.75	2000/2010	315	107 (335)	93 (86)	214 (456)	62[c] (170)**	12 (30)	0.45[e] (1.7)**		17.8		UNEP/MAP, 2013
Po, Italy	70.09	1914/2012	45,538	5 (45.7)	161 (387)	168 (1528)	38[d] (103)*	1.9 (36.2)	0.32[d] (6.1)*	113 (1947)	85	0.6	Cozzi et al., 2018
		2000/2010	47,250	6.4 (58.2)	168 (1520)	176 (1590)	142 (1290)	2.2 (45.2)			80		UNEP/MAP, 2013
Adige, Italy	11.95	2000/2010	6780	5.7 (39.7)	80 (556)	87.3 (605)	22.9 (159)	1.6 (24.8)			55		UNEP/MAP, 2013
Reno, Italy	4.93	2000/2010	1190	27.1 (91.5)	114 (385)	144 (486)	58.6 (187)	2.5 (19.3)			58		UNEP/MAP, 2013
Danube, Rumania	807.00	1931/2012	198,393	15 (37.2)	111 (275)	132 (327)		1.3 (7.1)		61 (302)	94	0.5	Cozzi et al., 2018

[a] Aounallah, 2016.
[b] El Boukhary, 2005.
[c] Pitta et al., 2014.
[d] Ludwig et al., 2009.
[e] Mattsson et al., 2009.
* The respective yield is calculated using the annual water discharge of Cozzi et al., 2018
** The respective yield is calculated using the annual water discharge of UNEP/MAP, 2013.
*** DIP values from (UNEP/MAP, 2013) are reported as PO_4.

2013). More importantly is that the multiyear mean ratio NH_4:NO_3 in terms of concentration in the Seybouse waters (122:33 μmol L^{-1} = 3.7) is about 60-fold that of the Mediterranean rivers (0.06, e.g. Ludwig et al., 2009). This implies that the Seybouse River estuary is heavily impacted by wastewater deliveries, whereas most Mediterranean rivers are rather enriched with NO_3, mainly originated from agricultural diffusive inputs (e.g. Garnier et al., 2010). N-NO_3 yields for the Po and Rhone Rivers, for example, are > 20-fold and 14-fold the Seybouse ones, respectively (e.g. Ludwig et al., 2009).

Apart from the heavy rainy years (2007 and 2009), that triggered significant water discharges, and the 2012 river flooding, the Seybouse had the lowest levels and yields of Si-Si$(OH)_4$ among the Mediterranean Rivers, as shown in Table 5. The lowering of Si$(OH)_4$ level in Algerian rivers was related to the reservoirs' retention, which can remove > 50% of the incoming flux (Ounissi and Bouchareb, 2013). Si$(OH)_4$ multiannual mean level for Seybouse River estuary was about one half the European and Mediterranean rivers, with a yielding three times lower (Dürr et al., 2011; Romero et al., 2013). The low levels of Si-Si$(OH)_4$ associated with elevated DIN levels resulted in unbalanced Si:N ratios in almost all years. Seybouse water deliveries always showed unbalanced Si:N ratios, similarly to the large rivers of the Mediterranean and the Black Sea, having values < 1 (Cozzi et al., 2018). The reduction in Si:N ratios could have many ecological and biogeochemical implications, as has been reported in many studies (e.g. Officer and Ryther, 1980; Justic et al., 1995; Turner et al., 1998). For example, diatoms become Si-limited when Si:N ratio falls below 1:1, which could lead to changes in both phytoplankton and zooplankton composition, coupled with eutrophication problems (Justic et al., 1995; Turner et al., 1998; Garnier et al., 2010).

Similarly to NH_4, the Seybouse river estuary displayed the highest levels of PO_4 compared to the Algerian and other Mediterranean rivers (Table 5). It however yielded moderate fluxes, as the most elevated levels occurred during the low river flow season, which brought only 16–18% the annual load. In addition, the flood event contributed only to about 25% of the P-PO_4 annual load. P-PO_4 yields were much higher than those of the contiguous Mafragh catchment and some European large rivers (Danube and Ebro Rivers), and rather comparable to that of the Rhône River (Ludwig et al., 2009; UNEP/MAP, 2013; Cozzi et al., 2018).

Interannual mean N:P ratios of Seybouse waters were generally above standard Redfield values but did not differ much from other NW Mediterranean rivers (e.g., Ludwig et al., 2009; Cozzi et al., 2018). Although the annual mean N:P ratios seemed to be approaching the balanced value (N:P = 16:1), most of the instantaneous values (samples) had N:P > 30 during high river flow and frequently displayed low N:P values (< 10) by dry season (Ounissi et al., 2014, 2016, 2018). Ounissi et al. (2018), for instance, reported that in spite of the fact that N:P mean value of 2014 appeared to be balanced (N:P = 16.7), almost all of the 54 samples showed unbalanced values.

Overall, the Seybouse River and its estuary were characterized by enhanced concentrations of NH_4, NO_2, and PO_4 during the dry period, which were indicative of wastewater pollution (Varkitzi et al., 2018). The importance of this source of anthropogenic nutrients decreased in the wet season, highlighted by the high levels of NO_3 and Si$(OH)_4$. Outflow of nutrient enriched waters to Annaba Bay could have had a severe impact on the productivity and phytoplankton composition of these waters.

The index of coastal eutrophication (ICEP) was introduced by Billen and Garnier (2007) to assess how much the river nutrient inputs can likely cause eutrophication in the receiving coastal water when N and P fluxes are delivered in excess over Si. The impact of the northwestern European rivers' input on the respective receiving coastal waters was tested by using the ICEP index (Romero et al., 2013). The authors compared whether seasonal trends in this eutrophication indicator match changes in northwestern European coastal phytoplankton, and found positive P-ICEP (excess in P over Si) values for most Mediterranean coasts, which means that phosphorus is limiting with regard to silicate in most river systems. They also reported N-ICEP (excess in N over Si) index positive values in almost all Mediterranean and Atlantic rivers, indicating a clear potential risk of eutrophication related to an excess of N over Si.

For the Seybouse River waters, the ICEP index values were positive in most cases, indicating a significant potential risk of eutrophication all around the year, except during and several weeks after the flood event of February 2012. The negative ICEP index values found during the flood and post-flood, which brought more Si$(OH)_4$ amounts compared to PO_4 and DIN, suggested less risk of eutrophication. The ICEP index positive values were sometimes related to N-ICEP or P-ICEP. The P-ICEP positive values were more frequent observed in low river flows, while N-ICEP ones were more frequent in moderate flows, except in June–July where NH_4 was heavily discharged over PO_4. This contrasts the findings of Garnier et al. (2010), who categorized most of the North African Rivers (including Seybouse River) within river systems having a less potential risk of eutrophication (based on N-ICEP calculated from Global NEWS data 2000).

Given the coincidence of the stratification period in the coastal waters of Annaba Bay (Ounissi et al., 1998; Frehi et al., 2007) with ICEP index positive values (more frequently observed in the dry and warm season), the eutrophication risk could largely be enhanced resulting in a high eutrophication level throughout the year, where blooms with harmful dinoflagellates are common (toxic and blooming species, Ounissi and Frehi, 1999; Frehi et al., 2007). Similarly, the blooming heterotrophic dinoflagellate *Noctiluca scintillans* in the Annaba Bay has been reported as a major component of the microbial community (Ounissi et al., 2016), where it developed in high numbers during the period of February–April. In addition, Ounissi et al. (2018) reported that the Seybouse estuary waters displayed high chlorophyll *a* values throughout the year (mean 21 μg L^{-1}), and exported large amounts of particulate matter (75 tons km^{-2} yr^{-1}), of which 3.4% were in the form of particulate organic carbon and about 1% in the form of biogenic silica.

Yet, the N and P dissolved organic forms (DON and DOP) have been addressed less frequently, despite their significant fraction and biogeochemical roles (Berman and Bronk, 2003; Rinker and Powell, 2006; Pitta et al., 2014). They can supply a significant fraction to N and P requirements during dinoflagellates blooms. Berman and Bronk (2003) reported that inputs of DON from heavily impacted rivers by human activity may stimulate the proliferation of toxic phytoplankton and eutrophication risk in the estuarine and coastal waters (Berg et al., 2001). In 2012 the Seybouse estuary's mean DON represented 10% of the TDN annual yield (20 kg N km^{-2}) and a mean level of 10.2 μmol L^{-1}, while the multiyear one reached 17.7 μmol L^{-1}, yielding 36.7 kg N km^{-2}. The DOP fraction within TDP annual yield was more important representing 20–25% (3.8 kg P km^{-2}), a value that could be comparable to the Mediterranean rivers (18.5%, Ludwig et al., 2009). In some other Algerian rivers, DOP annual yields were much higher than the estuary of Seybouse River, reaching 65–67 kg P km^{-2} (Table 5). In the Evros River, Greece, levels as high as 2–4 μmol L^{-1} for DOP and 30–40 μmol L^{-1} for DON were reported during the dry season (Pitta et al., 2014).

The lower Seybouse River waters were heavily enriched with dissolved N and P pools, and did not change substantially when crossing the estuarine part, in spite of some releases of NH_4 and PO_4 from direct untreated wastewater sewer and other minor urban domestic sources. Nutrient release from the bottom layer or the water-sediment interface could also be relevant in the shallow tidal rivers (e.g., Domingues et al., 2010; Falco et al., 2010), such as the Mediterranean estuaries. However, the highly stratified water column could limit vertical exchanges between the upper freshwater layer and the bottom marine water. This can result in the conservative behavior of nutrients passing through the estuary and flowing next to the sea in a very short time. The short residence time of the Seybouse estuarine waters could also help to maintain the conservative evolution of nutrients flowing into Annaba Bay. This was evidenced through the comparable levels and loads in the riverine and estuarine stations, with the exception of the DOP, which was stored in high rates within the estuary. The estuary removed 20.4 t yr^{-1} of DOP, and conversely released approximately an equivalent amount of P-PO_4 (Table 5). This might suggest that a relevant fraction of the stored DOP could have been re-mineralized in the form of PO_4 through bacterial degradation. A similar conversion of DON to DIN was tested on urban domestic water from Jiaozhou Bay, China, in the work of Li et al. (2019). The authors found that approximately 66% of land-based DON may contribute to DIN by microbial re-mineralization in Jiaozhou Bay. Furthermore, out of the direct urban domestic inputs, the high release of DIN within the Seybouse estuary (+385 t yr^{-1}) in parallel to the low amounts of DON might partially be related to the degradation of the bioavailable DON. Most of the released DIN amounts occurred during the dry period, when the estuary functioned like a saline Lake, with quasi-stagnant waters.

Overall, there is a severe lack of data on both DON and DOP along the Mediterranean rivers, even though over 40 years ago, Antia et al. (1980) wrote: 'we urge oceanographers and marine biologists to stop ignoring the role of DON in primary production'. Given the little information available about DON and DOP for the Mediterranean estuaries, it is difficult to validly weigh our findings and hypotheses about the fate or behavior of these important components within the Seybouse estuary and their potential effects on the marine adjacent coastal waters. Further biogeochemical investigations are needed on the main Seybouse River tributaries, including the estuarine part and its lower water layer which, apart from some of the salinity vertical distribution, is still completely unknown.

5. Conclusions

In this study, we assessed water discharges along with nutrient composition and loads entering both from the lower Seybouse River into its highly stratified estuary then from the latter into the Annaba Bay, in the context of the human impact on river-estuary-sea hydrological interactions. The year 2012 was relatively dry but had experienced a strong flooding event in late February, which had provided large freshwater discharges, heavily loaded with various dissolved nutrients, accounting for, 68%, 81%, 75%%, 62% and 25% of freshwater, Si-$Si(OH)_4$, N-NO_3, N-NH_4, and P-PO_4 the annual inputs, respectively.

The Seybouse catchment was characterized by the highest levels and yields of N-NH_4 and lowest levels and yields of N-NO_3 and Si-Si$(OH)_4$ compared to the Mediterranean rivers. The ratio NH_4:NO_3 in the Seybouse estuary's waters (3.7 in terms of levels) is about 60-fold that of the Mediterranean rivers, reflecting the strong non-point source influence on the lower Seybouse River estuary. Also, $Si(OH)_4$ mean level and yield in the Seybouse River estuary represented about one half and one third those of the Mediterranean rivers, respectively. In addition to the worsening of N:P ratios, the low levels of Si-$Si(OH)_4$ concomitant with high DIN levels resulted in unbalanced Si:N ratios (< 1) throughout the seasons. Annaba Bay was then subjected to highly polluted waters, from the Seybouse estuary, with significant NH_4 and PO_4 levels and very low $Si(OH)_4$ levels, besides the unbalanced Si:N:P ratios, which could have had a severe impact on the functioning and environmental conditions of its coastal waters. As depicted from the ICEP index, Annaba Bay experienced significant potential risk of eutrophication all around the year, except during and after several weeks of the flood event of February 2012. The potential risk of eutrophication was both related to P-ICEP, which was more frequent by low river flow and N-ICEP, which was more frequent by moderate flows, except in the driest period (June–July), when NH_4 was heavily discharged over PO_4.

By contrast to most Mediterranean and worldwide estuaries, the Seybouse estuary remained to receive/release nutrients up its outlet instead of removing/storing them. It experienced a positive budget relative to the incoming loads from the lower river reaches. An exception can be observed for DOP, which was trapped within the estuary at high rates and whose pattern remains unexplained. Its fraction within TDP was also much higher (20–25%) than DON within TDN (10%), but both elements still constituted relevant loads that should not be ignored in monitoring plans.

This study has advanced some of our knowledge on water and nutrient deliveries from the lower Seybouse River estuary and in particular the relevance of the flood events in reshaping the hydrological functioning of the estuarine part and its potential effects on the receiving coastal waters. We however still ignore a lot about the main Seybouse River tributaries and the estuary's lower water layer, which are still completely unknown, in spite of the upper freshwater layer and salinity vertical distribution. Further biogeochemical investigations, including dissolved and particulate organic matter, are needed on the entire Seybouse River catchment and its estuary.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2020.111231.

CRediT authorship contribution statement

Omar Ramzi Ziouch: Conceptualization, Formal analysis, Writing - original draft. **Hadjer Laskri:** Validation. **Houda Chenaker:** Visualization. **Nedjm Eddine Ledjedel:** Formal analysis, Data curation. **Tarek Daifallah:** Validation, Writing - review & editing, Software. **Makhlouf Ounissi:** Supervision, Methodology, Writing - review & editing.

Declaration of competing interest

We have no conflicts of interest to disclose.

Acknowledgments

This study was partially funded by the Algerian Ministry of Higher Education and Scientific Research under CNEPRU research project D00L03UN230120120003. We wish to thank the editor and the anonymous reviewers, whose comments and suggestions have clearly improved our manuscript. We thank Dr. R. Khelifa (Zurich University) and MS H. Naidja for improving the English writing of earlier versions of this manuscript.

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