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The Transmission Effectiveness of the Dissolved Nutrients (N, P, Si) Through a South Mediterranean Estuary (Seybouse, Algeria) Under Large Anthropogenic Forcing

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Abstract: The Seybouse Estuary (SE) is the downstream of the second great river in Algeria draining one of the main country's watersheds (6471 km^2, 1.5 million inhabitants). This study highlights the effect of the estuarine part on the distribution and the flux of dissolved nitrogen (N), phosphorus (P) and silicon (Si) through the SE. Surface water sampling was taken and analysed in the dry (September 2016) and wet (April 2017) seasons. Physical parameters and water discharge data were jointly recorded in parallel to sampling dates. Very low flows varying between 0.3 and 4.7 $m^3 s^{-1}$ were recorded at the outlet in dry and wet seasons, respectively. The SE outlet waters were 2.6 and 10 folds higher than upstream in dissolved inorganic nitrogen (DIN) and phosphates (PO_4) levels, respectively. However, the silicates (SiO_4) levels decreased by about 1/2 in the outlet waters. In terms of flux, the SE delivered to the coast 84 $t \cdot yr^{-1}$, 9 $t \cdot yr^{-1}$ and 56 $t \cdot yr^{-1}$ of DIN, PO_4 and SiO_4, respectively. The high DIN:PO_4 = 137 and low SiO_4:DIN = 0.52 molar ratios classify SE as one of the strong anthropised estuaries. The estuarine part amply modifies cycles and budgets of riverine nutrients introduced to the coast.

Key words: Nitrogen, phosphorus, silicon, outlet, estuary.

Introduction

Nutrients enter coastal waters via a diverse range of mechanisms including atmospheric deposition, groundwater seepage, catchment run off, wastewater and effluent discharge. Quantifying these various nutrient loads and managing their anthropogenic component is a huge challenge since the equilibrium of aquatic ecosystems near the coast is strongly influenced by the quantity and quality of the freshwater delivery (EEA, 2014; Wang et al., 2019). Thus, the protection of the water state within watersheds brings economic benefits by contributing to biocenoses protection, including coastal fisheries (Bao et al., 2022). Dali et al. (2023) emphasise that water resources to the Mediterranean Sea are scarce and anthropogenic pressure on rivers becomes particularly important. Moreover, the construction of dams on rivers and water abstraction for irrigation have evolved since the 1960s and have greatly reduced the river flow by at least 20% which has profoundly altered the natural functioning of Mediterranean rivers (Li et al., 2021; Ludwig et al., 2009).

Furthermore, estuaries and continental shelves occupy up to 5.2% of the earth's surface and 2% of the world's ocean volume. However, they support important economic activities: downstream dams, fisheries,

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aquaculture, navigation and transport. Currently, about 60% of the world's population lives along estuaries and coastlines (Wolanski, 2007). The estuaries are thus subjected to strong direct and indirect anthropogenic pressures. Besides, the estuaries are transition zones between the continent and the sea, characterised by intense processes of chemical, physical and biological exchange and transformation and thus constitute real filters for trapping and transformation of materials in transit (Ziouch et al., 2020). However, the water quality in these vulnerable areas is largely related to the high hydrological variability and the importance of anthropogenic impact in the watershed (Wang et al., 2019).

In the Mediterranean region, these hydro-systems are considered tidal rivers and are therefore little known as estuaries. In a local context, the estuaries of Algeria are not very well-known, and only a few have been explored, such as by Foudil-Bouras et al. (2011) for the Mazafran estuary, Fellah and Dali-Youcef (2014) for the Tafna estuary, Kies (2015) for the Cheliff estuary and Haridi et al. (2012), Ounissi et al. (2014, 2018, 2021) for the Mafrag Estuary. It should be emphasised that the totality of studies includes Aounallah (2015); Ziouch et al. (2020); Ounissi et al. (2008, 2014, 2021), who deal with the Seybouse are the ones who treat the estuary as a river. Thus, this work is mainly aimed at estimating the transmission effectiveness of N, P and Si across the Seybouse Estuary (SE) to the coastal waters.

Material and Methods

Presentation of the Study Area

The SE is located in the north-eastern of Algeria, with a length of 8 km (Ounissi et al., 2014), it extends from near the city of El Hadjar (36°47'55.87¨N, 7°46'27.60¨E) to its outlet (36°51'56.00¨N, 7°46'10.90¨E) located in Sidi Salem near the city of Annaba (Figure 1). It constitutes the downstream of the second great river in Algeria after Chélif River (ABH, 1999) with an average annual flow of 15 $m^3 s^{-1}$ (UNEP/MAP, 2013). Its watershed extends over 6500 km². Rainfall ranges on average between 450 mm in the south and 735 mm in the north (ABH, 2013). The Seybouse basin is populated with more than 1.5

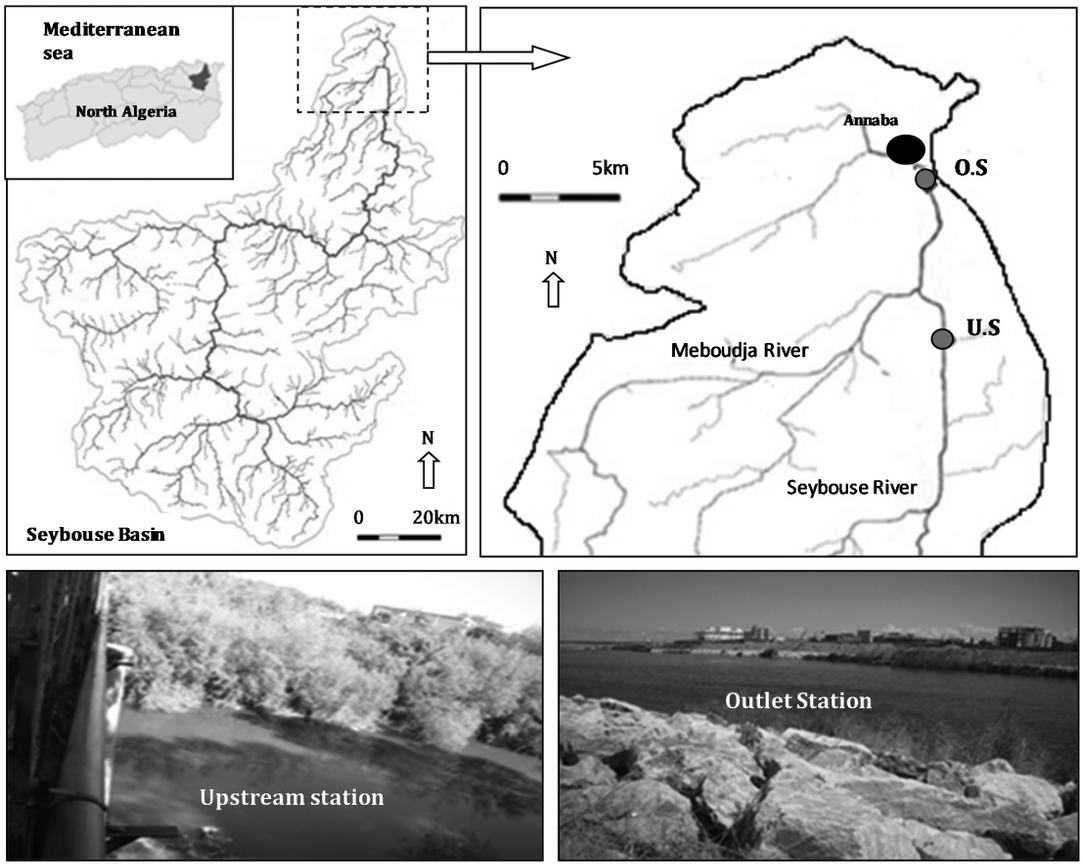

Figure 1: Study area and location of sampling stations. U.S: Upstream station; O.S: Outlet Station.

million inhabitants (ABH, 2013). Important agricultural activities are exerted which intensify from the inner basin to the littoral bung. According to UNEP/MAP (2013), the irrigated area in the Seybouse basin is about 3-4% of the total catchment area. ABH (1999) reported that the Seybouse River is largely regulated by multiple dams retaining approximately 400 hm³ (1/2 of the total annual runoff). The industries are mainly grouped in the sub-basin of maritime Seybouse. The most important is the industrial complex of El-Hadjar, which includes iron and steel plants, cement factory, paper and plastics factory and agri-food units and fertiliser production unit in Asmidal (Ziouch et al., 2020).

Analytical Methods

The SE was sampled at its respective upstream and outlet stations (Figure 1) in September 2016 for the dry season and April 2017 for the wet season. The readings of the temperature (°C), salinity (PSU) and electrical conductivity (µS cm^{-1}) were performed in situ using a Multiparameter WTW 197i. Measurements of water velocity were taken with a current meter type CM-2 (Toho Dentan Co. Ltd., Tokyo). Analyses of nutrients (Nitrogen: NH_4, NO_3, NO_2, Phosphorus: PO_4, Silicates: SiO_4) have been performed according to the protocols of Parsons et al. (1989), Aminot and Chaussepied (1983) and Rodier (1996). The flow at each station was determined according to the following equation:

$$\text{Flow } (m^3\ s^{-1}) = \text{Width (m)} \times \text{Depth (m)} \times \text{Current speed } (m\ s^{-1})$$

Instantaneous nutrient fluxes were calculated by multiplying their respective contents per river flow to obtain g s^{-1}. The annual flow of nutrients was estimated using the average of instantaneous flows (Preston et al., 1989).

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

where F is the annual flow (t.yr^{-1}), C_i is the concentration of the nutrients (µM, converted to kg m^{-3}), Q_i is the concomitant instantaneous flow ($m^3\ s^{-1}$ converted to $m^3\ d^{-1}$), 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.

Statistical Analysis

Principal Component Analysis (PCA) is used to determine the possible correlations between the 12 physicochemical parameters (variables) observed at the 2 stations representing the upstream and the outlet. The software used to perform the statistical analysis is Statgraphics Centurion XVIII trial version 18.1.11 (Statpoint Inc.; USA).

Results and Discussion

During the relatively dry year 2016/2017, the water flow at the SE outlet was on average 3.6 $m^3\ s^{-1}$ (Table 1), representing 1/2 and 1/10 of Seybouse water flows during the years 2008 and 2009, respectively (Ziouch, 2014). In contiguous catchments (Northeastern Algeria), Meddi et al. (2010) reported a decrease of at least 20% in total annual rainfall from the mid-1970s. River discharges with their loads of nutrients into the Mediterranean Sea were then doubly affected by the climatic variability and by the dam's retention.

Table 1: Seasonal variability of hydrological parameters upstream and at the outlet of the estuary

Season	*Physical parameter*	*Upstream*	*Outlet*
Dry	Temperature (°C)	25.4	26.7
	Salinity (PSU)	0.9	4.6
	Electrical Conductivity (µS cm^{-1})	2050	8120
	Flow ($m^3\ s^{-1}$)	0.5	0.1
Wet	Temperature (°C)	18.3	19.5
	Salinity (PSU)	1.2	1.9
	Electrical Conductivity (µS cm^{-1})	2560	3780
	Flow ($m^3\ s^{-1}$)	2	7

Table 2 shows that nutrient levels and loads vary remarkably at the spatiotemporal scale. The SE waters showed high levels of DIN throughout the seasons, it was on average 3 times higher at the outlet than upstream. While NO_2 ions formed a minor fraction within the DIN (4-16%), the SE waters were strongly dominated by NH_4 (53-82%) (Figure 2), which is unusual, compared to the major Mediterranean rivers where NO_3 dominates (Ludwig et al., 2009; UNEP/MAP, 2013). For Mediterranean rivers, EEA (2014) reported elevated values of NO_3 ranging from 20 to 376 µM. These contrasts are also observed in many contiguous Algerian river catchments (Ounissi and Bouchareb, 2013).

PO_4 ions reflected a clear trend and varied on average between 0.3 µM upstream and peaked more than 10 times higher at the outlet waters (Table 2). The high PO_4 levels suggest a strong influence of domestic wastewater

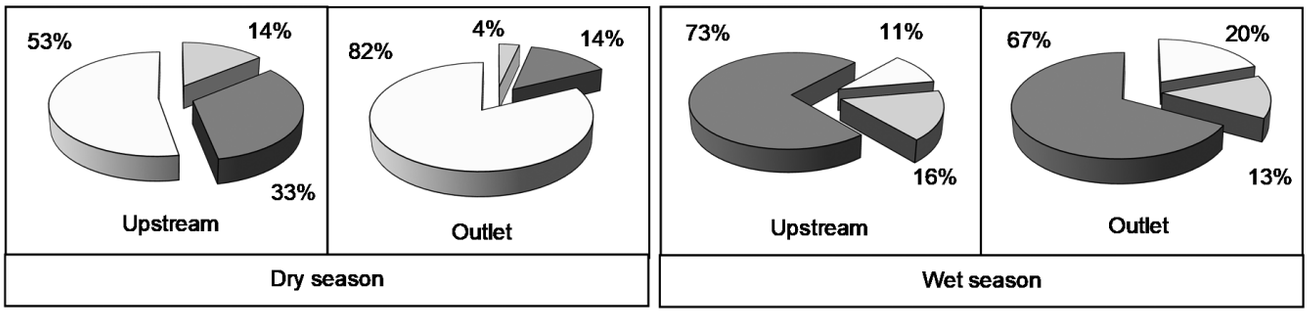

Figure 2: Distribution of DIN fractions in the SE during dry and wet season; □: NH_4, ■: NO_3, □:NO_2.

Table 2: Nutrient contents (µM), ratios, and fluxes ($t.yr^{-1}$) at the upstream and at the outlet of the SE in dry and wet season. DS: Dry season; WS; Wet season; Ups: Upstream station; Out: Outlet station; P/R: Production/Retention; (R%): Retention or production

		(µM)								*($t \cdot yr^{-1}$)*					
		NH_4	*NO_2*	*NO_3*	*DIN*	*PO_4*	*SiO_4*	*N/P*	*Si/N*	*NH_4*	*NO_2*	*NO_3*	*DIN*	*PO_4*	*SiO_4*
DS	Ups	29.8	7.9	18.5	56	0.4	82	156	1.5	6.6	1.8	4.1	12	0.18	36
	Out	205	8.7	35.5	250	3.6	40	69	0.2	9.1	0.4	1.6	11	0.35	3.6
	P/R	175	0.8	17	193	3.3	-42			2.5	-1.4	-2.5	-1.4	0.17	-33
	R%	589	9.8	92	343	903	-51			37.8	-78	-61	-11	94	-90
WS	Ups	7.2	11.2	49	68	0.2	68	295	1	6.4	9.9	34.7	60	0.45	120
	Out	27	7.8	39	74	2.7	43	27	0.6	83.6	24	121	229	18.6	264
	P/R	19.8	-3.4	-10	6.3	2.5	-25			77.2	14	86.5	169	18.3	145
	R%	275	-30	-21	9.2	1091	-37			1206	145	248	282	4033	121

which is consistent with the results of Ounissi et al. (2014, 2018).

Unlike anthropogenic origin elements, the SiO_4 highest contents were recorded upstream and the lowest ones at the outlet regardless of the season (Table 2). Masses of SiO_4 are already naturally reduced in our estuaries by low water flow and by the geological nature of rocks poor in Si (global average 150 µM; Tréguer et al., 1995). Silicon was moreover diminished by strong eliminations in dams (Durr et al., 2009; Ounissi and Bouchareb, 2013).

Nutrient budgets between upstream and outlet stations indicate that the SE functions as a producer of nutrients of anthropogenic origin and a consumer of natural origin (Table 2). These observations confirmed the findings of the PCA (Figure 3). Indeed, the factorial plan projection F1×F2 of the PCA indicates two segregated areas: Upstream station: Characterised by high levels of flow, NO_2, NO_3, SiO_4, N/P and Si/N which are the characteristics of pristine rivers, in contrast to the outlet station distinguished with high levels of Temp, Sal, EC, DIN, NH_4 and PO_4 resulting from the different anthropogenic activities in the estuarine part characterising the disturbed and anthropised estuaries.

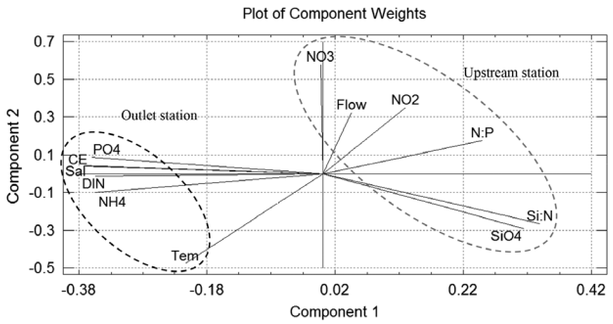

Figure 3: Factorial plan projection 1×2 of PCA of 12 variables (NH_4; NO_2; NO_3; DIN; PO_4; SiO_4; Flow; Temp; Sal; EC; N/P (DIN:PO_4) and Si/N (SiO_4:DIN)) from the Upstream and the Outlet stations.

Nutrient flux, which is proportional to the water discharge, varied largely into and from the SE (Table 2). Moderate flows as 3.6 $m^3\ s^{-1}$ contributed to discharge loads of only 229 $t \cdot yr^{-1}$, 18.6 $t \cdot yr^{-1}$ and 264 $t \cdot yr^{-1}$ for DIN, PO_4 and SiO_4, respectively; they appear very low compared to those of Mediterranean rivers (Ludwig et al., 2009; Romero et al., 2013) and Algerian rivers (Aounallah, 2015; Ounissi et al., 2014, 2021).

Furthermore, the algae need are satisfied with a molar ratio SiO_4:DIN:PO_4 = 16:16:1 (Redfield et al., 1963).

For the SE waters, DIN:PO_4 ratio was very high (137; Table 2) exceeding that of most Mediterranean rivers (Table 3).

Table 3: Mean values of the DIN:PO_4 ratio in some Mediterranean rivers

Mediterranean Rivers	*Country*	*DIN:PO_4*	*Reference*
Seyhan	Turkey	23	UNEP/MAP, 2013
Ceyhan	Turkey	64.5	UNEP/MAP, 2013
Axios	Greece	9.3	UNEP/MAP, 2013
Gallikos	Greece	54.5	UNEP/MAP, 2013
Krka	Croatia	71.3	UNEP/MAP, 2013
Neretva	Croatia	18.4	UNEP/MAP, 2013
Ebro	Spain	72	Cozzi et al., 2018
Ter	Spain	52	UNEP/MAP, 2013
Rhône	France	73	Cozzi et al., 2018
Argens	France	46	UNEP/MAP, 2013
Po	Italy	85	Cozzi et al., 2018
Reno	Italy	58	UNEP/MAP, 2013
Danube	Romania	94	Cozzi et al., 2018
Moulouya	Morocco	35.5	EEA, 2014
Seybouse	Algeria	137	This study

Besides, SiO_4:DIN ratio was balanced (1.3) upstream and low (SiO_4:DIN<1) at the outlet waters of the estuary regardless of the season. The level of anthropisation can be estimated from the SiO_4:DIN ratio. The low SiO_4:DIN ratio (0.52) compared with that of some world rivers, classifies the Seybouse among highly anthropised estuaries (Table 4).

It is finally understood that the estuarine part of the Seybouse is not just a transit channel but operated as a sink for SiO_4 and a source of DIN and PO_4 which amply modified the SiO_4:DIN:PO_4 ratio. This imbalance has major impacts on the functioning and productivity of coastal waters, this finding corroborates those reported worldwide (Bao et al., 2022; Justic et al., 1995). These hydrological studies should be a crucial element in decision support for integrated management of the SE and the Annaba coastline environments and their renewable resources.

Conclusion

Estuarine systems play a crucial role in the modifications of the biogeochemical cycles and budgets of nutrients from land to the sea. Water discharge of the SE varied between 0.1 $m^3 s^{-1}$ and 7 $m^3 s^{-1}$. This variability is linked to weather conditions as well as regulation by dams and abstraction by direct pumping of water from farm

Table 4: Mean values of SiO_4:DIN ratio in several prestine and anthropised world rivers and estuaries

Quality	*Rivers and estuaries*	*Country*	*SiO_4:DIN*	*Reference*
Prestine	Kebir Rhumel	Algeria	3.7	Ounissi and Bouchareb, 2013
	Kebir west	Algeria	4	Ounissi and Bouchareb, 2013
	Safsaf	Algeria	5	Ounissi and Bouchareb, 2013
	Mafragh	Algeria	2.12	Ounissi et al., 2014
	Amazone	South America	58.4	Vörösmarty et al., 1998
	Yokon	North America	32.9	Vörösmarty et al., 1998
	Mackenzie	Canada	20	Vörösmarty et al., 1998
	zaire	Congo	22.1	Vörösmarty et al., 1998
Anthropised	Ebro	Spain	0.7	Cozzi et al., 2018
	Rhône	France	0.6	Cozzi et al., 2018
	Po	Italy	0.6	Cozzi et al., 2018
	Danube	Rumania	0.5	Cozzi et al., 2018
	Mississipi	North America	0.9	Vörösmarty et al., 1998
	Po	Italy	0.7	Vörösmarty et al., 1998
	Rhine	Germany	0.4	Vörösmarty et al., 1998
	Seine	France	0.3	Vörösmarty et al., 1998
	Sybouse	Algeria	0.52	This study

lands to the banks of the Seybouse River for irrigation purposes. The SE delivered 162 µM of DIN in the wet season, from which NO_3 was the major component (70%) while in the dry season, it was the reduced form that dominated (68%), NO_2 always formed minimal fractions. PO_4 followed the same behaviour as DIN with high levels recorded at the outlet, while upstream it was only 1:10. Unlike anthropogenic origin elements, silicon varied on average between 75 µM and 42 µM upstream and at the outlet, respectively. The decrease in the SiO_4 levels can be related to the Silicon removal within the upstream reservoirs and other cascading filters but also to a biological removal in the estuarine part. In terms of flux, it delivered to the sea 84 $t \cdot yr^{-1}$, 9 $t \cdot yr^{-1}$ and 56 $t \cdot yr^{-1}$ of DIN, PO_4 and SiO_4, respectively. The SE appears to be more enriched in DIN than PO_4 and SiO_4. The DIN:PO_4 molar ratio seems to be very high (137) while SiO_4:DIN molar ratio was very low (0.52) which leads to qualifying Seybouse among the highly anthropised estuaries. The alteration of nutrient stoichiometry in SE waters could increase the potential of eutrophication risk across the Annaba coastal region. This study has advanced some of our knowledge of water inputs and nutrient biogeochemical changes through the SE and its potential effects on receiving coastal waters. Further biogeochemical investigations, including dissolved and particulate organic matter, over the entire Seybouse River watershed, its tributaries and its estuary are needed.

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