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Water and nutrient fluxes from three coastal Mediterranean Rivers (N-E Algeria)

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Abstract

The objectives of the present study were to estimate water delivery and dissolved nutrients loads (nitrogen N, phosphorus P and silicates Si) from three minors coastal rivers (about 14% of Algerian coastal watersheds). Freshwater flow dissolved inorganic nitrogen DIN (NH_4, NO_3 and NO_2), dissolved organic nitrogen DON, dissolved inorganic phosphorus DIP, phosphate (PO_4), dissolved organic phosphorus DOP and silicates SiO_4 were measured monthly at River outlet in the year 2011. The rivers were characterized by high values of ammonia (NH_4) and phosphate (PO_4) which reveal the dominance of organic and domestic pollutions. In contrast, values of SiO_4 were very low and will be in relation to the retention in dams. Dissolved nitrogen loads varied considerably from 43 to 227 kg/km²/y where DON formed 20 to 40%. Loads of total dissolved phosphorus (TDP) fluctuated in the range of 20- 80 kg/km²/y in which the organic fraction forms largely dominated (51 to 74%). At River outlets, the loading ratio of nutrients (Si: N: P) were altered by agricultural and household wastes. Here, Si:N and N:P mass ratios ranged from 3-6 and 10-20 respectively, indicating large N and P inputs. These biogeochemical conditions would induce deep impacts on the ecology and the productivity of the adjacent coastal waters.

Keywords: Nutrients, discharges, ratio, River, Mediterranean, Algeria.

1. Introduction

The marine ecosystem functioning is considerably influenced by the freshwater received to the seas, through their control on the general water circulation in the Mediterranean Sea (Skliris et al., 2007). In last decades, humans activities have widely transformed the hydrology of coastal rivers by perturbing their overflow in artificial reservoirs. Also, the immoderate employ of fertilizers from agricultural and domestic wastes have altered the chemistry of freshwater delivery into the sea that affected the nearby coastal ecosystems (Howarth et al., 1996; Meybeck, 2003; Turner et al., 2003; Nixon et al., 2003; Liu et al., 2008). Furthermore according to Margat and Treyer (2004), water and related constituents discharged by rivers of to the Mediterranean Sea undertook important changes during latest decades; principally water resources in the Mediterranean are limited and anthropogenic pressures on rivers are very significant. The hydrological stability, dissolved nutrients (nitrogen or N, phosphorus or P, silica or Si), carbon, sediment and biodiversity of water surfaces are mainly controlled by the transfer of river materials to the sea (Meybeck, 2003). Inaddition to their hydrological role, the rivers are recognized to play a particular role in supporting the production of the Mediterranean Sea where the productive regions are restricted to the bordering coast (Bosc et *al.*, 2004). The adjustments in river discharge and

nutrient entrance are established to be central in controlling the productivity and the functioning of the marine environment. Geochemical modifications of nutrient loading to coastal waters influence negatively human health and environment, for example damage of habitat and biodiversity, eutrophication and expand in blooms of some species of harmful algae, fish kills and hypoxia (Cloern et *al*., 2001; Ragueneau et *al*., 2006; Billen and Garnier, 2007; Howarth et *al*., 1996; Rabalais, 2002). Moreover, Rabalais and Turner (2001) and Turner *et al*. (2003) elucidated surprising impacts resulting from modifications occurring at the global scale and are now far upstream. Further data on coastal catchments of Algeria regarding water discharges and fluxes of N, P and Si is missing, excepting some works of Khélifi-Touhami M et *al.* (2006) and Ounissi M and Bouchareb N (2013). In addition, the assessments of nutrient inputs from both atmospheric and riverine sources into Mediterranean waters are still rare especially in southwestern Mediterranean regions (Ounissi et all 2018).
In view of the severe lack of geochemical data for coastal river basins, the aim of the present work is to evaluate water and nutrient loadings of N, P and Si in three representative coastal catchments of Algeria.

2. Materials and methods

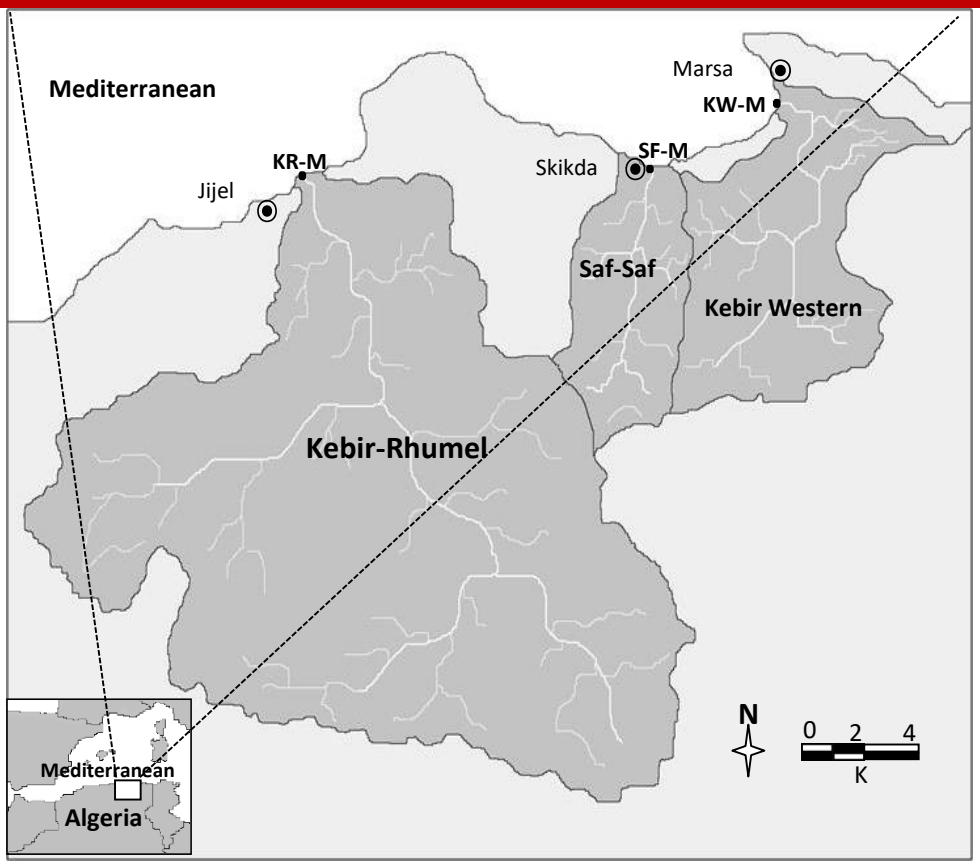
2.1. Study area

The three watersheds of the studied rivers have a total surface of 1, 1160 km² with a population of about two Millions and are mainly submitted to domestic and agricultural wastes (Fig. 1). They are heavily managed by numerous dams that retain more than the half ofthe precipitation wealth. In the Kebir-Rhumel (KR) catchment is arranged by the Beni- Haroun dams (one Billion m³ water), however that is populated by approximately 1 Million inhabitants. On the other hand the catchment of Kebir Western (KW) is arranged by the Zit- Amba dam of a capacity of (50 million m³) and gathers only 30.000 inhabitants. Also the Safsaf (SF) catchment is controlled by the Zardaza dam of a capacity of (120 million m³) and gathers approximately of 70.000 inhabitants. The catchments receive an annual precipitation yield of about 400-800 mm inducing large fluctuation in river flow. In summer period all rivers fall almost dry at the entering of dams while at the exit the dams continue to deliver lowflows. Being irrigated from dams and near-river mouths, the northern areas sustain large intensive agricultural activities and the land use becomes mainly dominated by intensive agricultural practices and forests occupied always less than 20%.

2.2. Methods

Flow velocities of the estuarine water, at the moment of sampling from the same water mass, were assessed with the current meter CM-2 (Toho Dentan Co.Ltd, Tokyo). The flow rate ($m^3\ s^{-1}$) was calculated by multiplying the water velocity ($m\ s^{-1}$) by the total surface area (m^2) of the estuary's transecting at the mouth station. Water salinity and temperature measurements were taken with the multiparameter probe WTW 197i. Two liters of water from the middle of the flow were collected for nutrient analysis. Water samples for nutrient analyses were frozen in polyethylene bottles and processed within two days from collection. In the laboratory, after filtration of the sample through Whatman GF/C glass filters (0.5µm porosity), dissolved inorganic nitrogen DIN (NH_4, NO_3, NO_2), dissolved organic nitrogen DON and silicates (SiO_4) were determined by means of standard colorimetric methods described in Parsons and al. (1989). Total dissolved phosphorus TDP, polyphosphate P_2O_5, and dissolved organic phosphorus DOP were determined following the standard method of Rodier (1998).

Figure 1.



Sampling stations in the coastal Rivers of Kebir-Rhumel (KR), Kebir West (KW) and Safsaf (SF): KR-M: mouth of KR River; KW-M: mouth of KW River; SF-M: mouth of SF River.

All hydrological parameters and nutrients were measured monthly from March 2011 toFebruary 2012 in one stations for each Rivers KR, KW and SF respectively (Fig. 1). The instantaneous flux of nutrients was calculated by multiplying their concentrations by the estuary flow. The annual loads for nutrients were estimated using the method of average instantaneous loads (Preston et al., 1989):

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

where F is the annual load (tons/years), Ci is the concentration of nutrients (µM converted to kg m^{-3}), Qi is the concomitant instantaneous flow (m^3 s^{-1} converted to m^3 day^{-1}), n is the number of days with concentration and flow data and K is the conversion factor to consider the period (365 days) and unit of estimation.

3. Results and discussion

3.1. Physical parameters deliveries at the rivers' outlets

The quantity of fresh water discharged to the sea varies according to the river between 258.10^6 and 536.10^6 m^3/y (Tab. 1). On the other hand water flowing to the sea accompanied by significant quantity of suspended materials where vary according to the river between 13519 t/y and 149401 t/y (Tab. 1). Concerning dissolved solids (TSS) and electrical conductivity (EC) they range in order between 365 mg/l and 467 mg/l for TSS and 902 (µs/cm) and 1014 (µs/cm) (Tab. 1) , All the Rivers studied represent an important variation of water discharges and precipitation (between 400-600mm) this variability of water mass

depends on the climate and water retention in the dams of a share and in addition it is influenced directly by the loadings of the nutrients.

Table 1. Mean and standard error (±) of electrical conductivity (EC), total dissolved solids (TDS) and flows at river outlets and water flow.

	EC (µs/cm)	TDS (mg/l)	Flow (m^3/s)	TSS delivery (t/y)	Water delivery (10^6 m^3)
Outlet KR	1014±311	467±165	17±15	149401	536
Outlet KW	916±158	365±58	13.5±8	13519	409
Outlet SF	902±293	364±110	8.2±4.7	19685	258

3.3. Nutrients loadings at river outlets

Nutrient fluxes and specific loadings from the studied Rivers are shown in the Table 2. Mediterranean rivers are characterized by large variations in River flow. River export of the forms of TDN, TDP and of SiO_4 increased in the KR mouth during the period compared with KW and SF, the high level of nutrients could be explained by the human activity in the KR basin compared with KW and SF (Ounissi M and Bouchareb N 2013). The input by all Rivers represents about 78-91% of the inorganic forms (DIN) and 26-49% of the (DIP) (Tab. 2). For dissolved organic forms (DON and DOP), the major fluxes can be observed in the KR River with a fraction of 52-60% respectively of total contribution of all the basins. In term of specific loadings, the small watersheds of KW and SF deliver to the sea considerable masses of PO_4 and NH_4 (19 to 22kg P-PO_4/km^2/y and 57 to 78kg N-NH_4/km^2/y) in comparison to the large watershed of KR characterizing the biggest dam of Algeria (Tab. 2). According to Ludwig et al. (2009), these quantities can represent one of the high ratios in Mediterranean rivers. An important quantity of Si was introduced to coastal water (338 to 520kg SiO_4/ km^2/y), and weakest flow specific is in the SF River is remarked compared has them in addition to basin studied with a value of (125kg SiO_4 km^2/y). The specific loadings of DIN were however low in KR watershed (27kg N/km^2/y) than 70% of the major Mediterranean rivers as reported by (Ludwig et al., 2009) compared to strong value in the SF and KW (130to 185kg N/km^2/y). The large amount of the DON brought to coastal water ranged between (53 to 131 t/y) suggests that organic nitrogen inputs may contribute markedly to marine eutrophication than was previously assumed, as already established by Seitzinger and Sanders, (1997). In the same way, the fluxes introduced to the coastal zone showed that DIN: PO_4 and Si: PO_4 ratios were frequently superior to the Redfield ratios values, suggesting thatP may be the limiting factor for phytoplankton growth. The N: P ratios increased greatly since the rise of agricultural practices and the latest reduction of phosphates in washing powders. Thus, the production of phytoplankton in coastal marine would be essentially controlled by P, which is the limiting nutrient at the river mouths. The alteration of Si: N ratios becomes a worldwide problematic as indicated in the data (Bernard et al., 2010; Ragueneau et al., 2006; Hamburg et al., 2008).

Table 2. Annual fluxes of nutrients at rivers outlets. Specific loadings (kg/km^2/y) are given between parentheses.

	NH_4 (t/y)	NO_2 (t/y)	NO_3 (t/y)	DIN (t/y)	DON (t/y)	TDN (t/y)	PO_4 (t/y)	P_2O_5 (t/y)	DIP (t/y)	DOP (t/y)	TDP (t/y)	SiO_4 (t/y)	N :P (g/g)	Si :N (g/g)	Si :P (g/g)
KR	82	23	108	213	131	344	32	15.5	47	136	183	1011	20	6	87
	(11)	(3)	(13)	(27)	(16)	(43)	(4)	(2)	(6)	(17)	(23)	(125)			
KW	109	32	107	248	68	316	36	23	59	95	154	988	21	5	72
	(57)	(17)	(56)	(130)	(36)	(166)	(19)	(12)	(31)	(50)	(81)	(520)			
SF	97	20	114	231	53	284	28	6	34	35	69	485	10	3	24
	(78)	(16)	(91)	(185)	(42)	(227)	(22)	(5)	(27)	(28)	(55)	(388)			

4. Conclusion

In conclusion, it can be stated that the major characteristics of the river that formed the subject of this study are marked by conditions of strong enrichments in particular in NH_4 and PO_4 contrary to the SiO_4. Overall, the water and nutrient transfer in the coastal rivers can be summarized as follows:

- The high level of nutrients could be explained by the human activity in the KR basin compared with KW and SF.
- Water mass flow varies depends on the climate and water retention in the dams of a share and in addition it is influenced directly by the loadings of the nutrients.
- The rivers were characterized by high values of ammonia (NH_4) and phosphate (PO_4) which reveal the dominance of organic and domestic pollutions.
- The loading ratio of nutrients (Si: N: P) were altered by agricultural and household wastes.

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