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Intitulé

Nutrient loading from three eastern streams (Kebir-Rhumel, Kebir West and Saf-Saf) Effects of dams on water, sediment and nutrient retentions

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RESULTS

ABSTRACTS

Beni-Haroun dam

Abstract

Nutrient and particulate material distributions and fluxes into and from the dams and into coastal waters from three streams' mouths (Kebir-Rhumel; Kebir West and Saf-Saf) were assessed during January 2012-April 2013 in three stations for each stream catchment. The stations were located at the entrance and the exit of each dam (Beni-Haroun; Zit Amba and Zerdaza) and at each stream's mouth. The streams' waters were heavily charged with NH_4 and PO_4, even at the dams' entrances, by contrast to $Si(OH)_4$ levels that still low. From the incoming fluxes of inorganic nutrients, the dams trapped annually 29-86%, depending on the nutrient, but in terms of concentration the dams released great levels of the dissolved organic forms (DON and DOP) and particulate organic matter forms (POC, BSi). At catchment scale the TDN yield reached 333 kg $km^{-2}yr^{-1}$, in which the organic fraction formed 33%, while that of TDP reached 85 kg $km^{-2}yr^{-1}$, with a great organic fraction. The POC yield was 1413 kg $km^{-2}yr^{-1}$, while the yield of BSi was 32 kg km^{-2} yr^{-1}. At the streams' mouths the Si:N ratio decreased while N:P ratio increased indicating large inputs of N over P and Si at the lower catchments. The streams introduced into the neighboring coastal waters high masses of suspended sediments, accounting up to 104 t $km^{-2}yr^{-1}$of soil erosion. Strong soil salts loss (up to1439 kg km^{-2} yr^{-1}) affected the fertility of the top soil catchments. The flood event of late February 2012 contributed to about third the annual water discharge, sediment, dissolved salts and nutrients load. Despite the lowering of the nutrient inputs into the coastal waters, the catchments were heavily impacted in several ways: high levels in NH_4 and PO_4; lowering of $Si(OH)_4$ levels; lowering of water flow behind dams; high soil erosion rates. These hydrological and biogeochemical changes would have severe economic and ecological impacts on both the catchment waters and soil wealth and the functioning and the productivity of the land-marine system.

Keywords: *stream; catchment; N:P; Si:N; TSS; POC; BSi; Beni-Haroun dam; dam retention*

Résumé

La distribution et les flux de nutriments entrant et sortant des barrages et à l'embouchure de trois cours d'eau côtières (Kebir-Rhumel, Kebir Ouest et Saf-Saf) ont été évalués durant la période d'étude (Janvier 2012- Avril 2013) à partir de trois stations aux embouchures et de deux stations représentant l'amont et l'aval de chacun des trois barrages (Beni-Haroun, Zit-Amba et Zerdaza). Les cours d'eau se caractérisent principalement par des fortes teneurs en NH_4 et en PO_4, même avant d'aboutir aux barrages, à la différence de $Si(OH)_4$ dont la teneur est déjà réduite en amont. A partir du flux minéral reçu à l'amont, les barrages retiennent annuellement 29 à 86% selon l'élément. Mais en terme de concentration les barrages libèrent à leurs avals des eaux fortement chargées en matières organiques dissoutes (NOD, POD) et en matière organique particulaire (COP, BSi). A l'échelle du bassin versant, les flux spécifiques de l'azote dissous atteignent 333 kg km^{-2} an^{-1}, au sein duquel la fraction organique représente jusqu'à 33 %, cependant que celui du phosphore dissous n'excède pas 85 kg $km^{-2}an^{-1}$, avec une dominance de la fraction organique .Les flux spécifiques de matière organique particulaire en COP atteignent 1013 kg $km^{-2}an^{-1}$,au sein duquel la fraction zooplanktonique COP2 représente jusqu'à 51%, cependant que celui du silicium biogénique n'excède pas 32 kg km^{-2} an^{-1}. Aux embouchures, Si:N diminue, mais N:P s'accroît, indiquant d'importants apports en N relativement au P dans le bas des bassins. Les cours d'eau introduisent à la mer d'importantes masses de sédiments en suspension correspondant à un taux d'érosion des sols de bassins de 104 kg km^{-2} an^{-1}. Une forte perte de sels dans le sol (jusqu'à 1439 kg km^{-2} an^{-1}) a affecté la fertilité du sol supérieur des bassins versants. L'inondation de fin février 2012 a contribué à environ le tiers des rejets annuels d'eau, de sédiments, de sels dissous et de nutriments. On considère ainsi que l'ensemble des bassins est fortement anthropisé à plusieurs titres :fortes teneurs en NH_4, PO_4, réduction des teneurs en $Si(OH)_4$, Production élevée de POC et BSi dans la sortie des barrages, déséquilibre des rapports Si :N :P, faibles débits à l'aval des barrages, fortes érosions des sols, salinisation des barrages et des sols des bassins, faibles apports en nutriments à la mer. Ces multiples changements biogéochimiques auront un impact écologique sur le fonctionnement et la productivité des barrages et du système du continent marin.

Mots-clés : *rivière, bassin versant, N:P, Si:N, barrage Beni Haroun, TSS, COP, BSi, rétention*

الملخص

تم تقييم توزيع المواد الغذائية والتدفقات من وإلى السدود والى المياه الساحلية من ثلاثة مجاري الانهار (الشمال الشرقي الجزائري) خلال فترة جانفي 2012 الى افريل 2013 في ثلاث محطات في كل نهر (كبير الرمال، الواد الكبير والصفصاف). عند مدخل ومخرج كل من السدود (بني هارون، زيت العنبة و زردازة) وعند مصب النهر .وكانت الخصائص الرئيسية للأنهار مستويات عالية من (NH_4, PO_4) حتى في مداخل السدود ، بعكس مستويات [$Si(OH)_4$] التي لا تزال منخفضة حتى في مدخل السدود. من التدفقات الواردة المواد الغذائية غير العضوية، تحتفظ السدود سنويا ب 29-86٪ بحسب المواد الغذائية، ولكن تنتج مستويات كبيرة من الأشكال العضوية (DOP, DON) و المواد العضوية الجسيمية (POC , BSi) في مخارج السدود من حيث التركيز. على نطاق الاحواض ، تركيزات النيتروجين المذاب تصل قيمتها إلى 333 طن/ كلم² سنة، حيث تصل نسبة الجزء العضوي إلى 33٪، في حين أن الفوسفور الذائب تصل قيمته الى 85 طن/ كلم² سنة، مع هيمنة الجزء العضوي.،قيمة تدفقات المواد العضوية المتمثلة في (POC) تصل إلى 1413 /كلم² سنة، والتي يشكل فيها جزء العوالق الحيوانية,(POC 2) ما يصل إلى 51٪، في حين أن قيمة السيليكون الاحيائية تصل إلى 32 طن/كلم² سنة. انخفاض نسبة (S/N) بينما ارتفعت نسب (N/P) عند مصبات النهر،و هذا يشير إلى مدخلات كبيرة من N بالنسبة P في مصبات الاحواض المائية .الأنهار أدخلت الى مياه البحر المجاورة نسب مرتفعة من الرواسب العالقة و المقدرة ب 14-104 طن/ كلم² سنة من تاكل التربة وقد أثرت خسارة أملاح التربة القوية (حتى 1439/ كغ/ كم ^{2} سنة) على خصوبة مستجمعات التربة العليا. وساهم حدث الفيضانات الذي وقع في أواخر شباط / فبراير 2012 في حوالي ثلث التصريف السنوي للمياه والرواسب والأملاح الذائبة وحمل المغذيات.. واذا نعتبر أن مجموع الاحواض المائية تأثر بشكل كبير بعدة طرق: مستويات عالية في (NH_4) و (PO_4) خفض مستويات $Si(OH)_4$,تركيزات عالية من (POC) (BSi) عند مخارج السدود؛ انخفاض تدفق المياه عند مخارج السدود، معدلات تآكل التربة عالية , ملوحة السدود و اراضي الاحواض ,إنخفاض المدخلات من المغذيات إلى المياه الساحلية. هذه التغييرات البيوجيوكيميائية سيكون لها بعض الأثر البيئي على أداء وإنتاجية السدود ونظام القارات البحرية على حد السواء.

الكلمات المفتاحية مجرى النهر, الحوض, سد بني هارون,الكربون,السليكا الاحيائية, المادة المذابة

INTRODUCTION

Introduction

During the recent decades water resources have been subject to various anthropogenic disturbances, including irrigation, dam retention and other needs of the population (Vörösmarty and Sahagian, 2000). To meet the growing water needs, numerous dams have been built all around the Mediterranean Sea (Lehner et al., 2011). Mediterranean rivers fluxes are then experiencing large reduction by at least 20 % over the last 40 years (Ludwig et al., 2009). The construction of dams and other water structures to meet human needs will also have negative impacts on the diversity and productivity of coastal marine waters (Conley et al., 2000; Nixon et al., 2004). Dams may have a strong impact on the water and nutrient river discharge due to silicon (Si) and phosphorus (P) retention within sediments (Aviles and Niell., 2007; Durr et al., 2009).

Nitrogen (N), P and Si are crucial elements for maintaining biological productivity in aquatic environments. Inputs of these dissolved nutrients from coastal catchments to the receiving coastal waters have increased dramatically as a result of intensified urban development, agriculture, and industrialization (Levin et al., 2015; Durrieu de Madron et al., 2011; Ludwig et al., 2009). The decrease in Si in the coastal waters has modified the composition of the phytoplankton by favoring the non-demanding species (often harmful dinophytes) to the detriment of the diatom species (Ittekkot et al., 2000). The relationship between algal biomass and nutrient loading is now well established for estuaries and freshwater ecosystems (Howarth and Marino, 2006; Perran et al., 2009). Ludwig et al. (2009) reported that the decrease in Si fluxes from rivers to the Mediterranean is rather related to reducing river flows heavily regulated by dams. Silica is also a major component of the total dissolved solids found in continental waters resulting from the chemical weathering of soils and surficial rocks. As such, it provides information on weathering processes and rates (Wollast and Mackenzie, 1983; Gaillardet et al., 1999). Approximately 87% of earth's land surface is connected to the oceans by rivers (Ludwig and Probst, 1998); rivers discharge many different forms of nutrient elements, including organic and inorganic species in dissolved and particulate form (Liu et al., 2009). Rivers discharge into marine environment, was estimate to be 35000 $km^3\ yr^{-1}$ (Milliman, 2001) and loads of sediment reaches $18{\times}10^{12}$ tons per year (Milliman and Syvitski, 1992; Ludwig and Probst, 1998; Syvitski, 2003). In addition to the changes in amounts and forms (dissolved inorganic, organic, particulate) of riverine nutrients, their ratios (Redfield ratios: N:P:Si = 15:1:20) have received much attention as a predictor of phytoplankton composition changes and production rate, both globally and regionally (Redfield et al., 1963; Turner et al., 1998, 2003; Chai et al., 2009; Elser et al., 2009). Diatoms, a type of unicellular algae, are responsible for as much as 30–40% of the primary production occurring in the surface ocean, and even a greater percentage of the organic-carbon flux exported from the euphotic zone (Buesseler, 1998). These siliceous phytoplankton forms are known to play a major role in the downward export of organic carbon (Goldman, 1988) and to drive most of the removal of biogenic silica (Si) from surface waters in the ocean (Michel et al., 2002). Dissolution of biogenic silica (BSi) in coastal environments is important for marine productivity. Understanding this process is central to assessing the global silicon cycle, which is closely linked to the global carbon cycle (Wu et al., 2015). Biogenic silica (BSi) is produced in the upper ocean by siliceous organisms, primarily diatoms (Wu et al., 2015). The global average benthic silicic acid flux at the sediment–water interface is approximately an order of magnitude greater than the amount that of riverine input (Tréguer and De La Rocha, 2013). Freshwater diatoms, living and as detritus, are also considered as BSi (De Master, 2003).

Rivers play an important role in the global biogeochemical cycles by transferring dissolved and particulate substances from land to sea. By creating reservoirs in rivers, humans are substantially impacting the flux of sediments, organic matter and nutrients to the coastal zone (Vörösmarty et al., 2003). The rivers play a particular role in supporting the Mediterranean production whose most productive zones are limited at the adjacent coast (Friedl, 2004; Teodoru, 2006). Jointly to the reduction of the discharge and the silicon retained in large proportions in the dams, the fluxes in nitrogen (N) and in phosphorus have increased 3-5 times (Meybeck, 2003; Ludwig et al., 2009) and the Si:N:P ratios altered. Urban and agricultural nutrient inputs and water residence time within reservoirs also lead to change the nutrients Redfield ratios (Ludwig et al., 2009). In addition, most studies about impacts of reservoir and river export of nutrients to the sea did not take into account organic compounds. However, some studies reveal that, even if the dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) are important components of riverine inputs and coastal catchments (Purvina et al., 2010; Wiegner et al., 2006), they are rarely considered within nutrient loadings pool. For example, Wiegner et al. (2006) reported that DON often dominates the total dissolved nitrogen (TDN), but yet it is not considered to affect coastal water quality because it is assumed to be refractory. The authors add that DON needs to be considered into coastal nitrogen loading budgets, because of its rapid bioavailability as well as its atmospheric deposition in watersheds that forms about 15–30 % of the total bioavailable dissolved nitrogen (Whitall and Paerl, 2001). In addition, data on river nutrient loading to the Mediterranean catchments are also scarce and are missing in the Southern Mediterranean countries (Ibanez et al., 2008; Ludwig et al., 2009) despite the works of (Ounissi and Bouchareb (2013); Taamallah et al., 2016).

In Algeria the surface water yield is very limited, about only 12 km^3 of which 7 km^3 are retained in the dams (Benblidia and Thivet, 2010). In addition to the direct degradation, dam's construction, mainly used to irrigate about a million hectares of Algerian agricultural land (Benblidia and Thivet, 2010), the cycle of the water basin scale is modified. In Algeria, investment infrastructure for water mobilization, supply and transfer currently represent 2% of the GDP. The construction of more than 30 dams over the past decade has increased the storage capacity of surface water to approximately 7 10^9 m^3 (Benblidia, 2011; Remini, 2010). On another hydrological level, Algeria has natural resources limited, irregular and very unequally distributed. About 90% of all Surface runoff estimated at 12.4 10^9 m^3/year, can be found in the coastal region (Benblidia, 2011).

This work is part of a project (National Program on Environment and Promotion of Sustainable Development under the N°4/u23/523. It aimed at evaluating the distribution and fluxes of water, sediment and nutrients (N, P, Si) to the sea through the main coastal river basins covering about 70% of the Algerian coastal basins. This study is also a continuity of the Boucharb's thesis (Bouchareb, 2013; Ounissi and Bouchareb, 2013), which focused on the rivers nutrient flux from Kebir-Rhumel, Kebir West and Saf-Saf. In addition the effects of dams on the biogeochemistry of N, P and Si, sediment and water and plankton (in the form of biogenic silicon and particulate organic carbon) have been largely considered.

The objective of this study were to assess (1) the distribution of silicon, nitrogen and phosphorus in the catchments studied for geochemical transfers at the river/sea interface, (2) to determine the effects of dams retention on sediment, water and nutrient, and (3) to evaluate the water, sediment, nutrient and particulate matter (particulate organic carbon and silicon biogenic) fluxes into the adjacent coastal area.

This thesis is organized accordance to the objectives. After the present introduction, we review the available information and data on the hydrology and surface water chemistry in the Mediterranean in particular. The manuscript is structured in five chapters. The first chapter presents is strictly documentary, which defines and gives the main biogeochemical characteristics of all the studied materials (water and rivers, total suspended solids (TSS), Total dissolved solids (TDS), N, P, Si, POC (particulate organic carbon), BSi). The second chapter provides the main geographical characteristics of the basins studied and the sampling strategy. It also presents the methods of biogeochemical analyses and estimation of nutrient fluxes. The third chapter presents the results of the hydrology, nutrient and particulate material concentrations and loads for the Kebir-Rhumel catchment. The fourth chapter presents water discharge, sediment, particulate matter and nutrient concentrations and fluxes for the Kebir West catchment. The fifth and last chapter presents the variation of water discharge, particulate matter and nutrients concentration and fluxes for the Saf-Saf catchment. The thesis continues with a discussion that provides the fundamental results, ponders and situates the whole of the results in the context of the starting problematic. We especially emphasized on the role of dams in biogeochemical changes of nutrients and dissolved and particulate matter. The work ends with the conclusions which summarizing the most relevant findings. Some data of Kebir West catchment have been published in two small journals cited in Scopus data base. The two articles are given at the end of the manuscript.

CHAPTER I

CHAPTER I: WATER, SEDIMENT AND NUTRINETS IN COASTAL CATCHMENTS

1. Presentation and biogeochemical roles of riverine materials

1.1. Water and River

Water is the most essential substance for all life on earth and a precious resource for human civilization (Qu et al., 2013). Coastal zones with their resources are important for the development of human activities and are major contributors to economic prosperity, social wellbeing and quality of life; as their exploitation represents the major income for coastal people, through fisheries, agriculture and tourism, as the Mediterranean has become the greatest tourist destination in the world (Turley, 1999). Disturbance of the hydrologic cycle has received significant attention with respect to land–atmosphere exchanges, plant physiology, net primary production, and the cycling of major nutrients (Foley et al., 1996, Sellers et al., 1996; McGuire et al., 1997). Changes in land use are also recognized as critical factors governing the future availability of fresh water (Chase et al., 2000).

Humans have built dams and impoundments for thousands of years for various purposes, including flood control, water supply, irrigation, recreation, navigation, and the generation of hydropower (WCD, 2000). In addition, the construction of dams on rivers and the removal of water for irrigation have evolved since the 1960 and have greatly reduced flow River by at least 20%, which has profoundly changed the natural functioning of Mediterranean rivers (Humburg et al., 2008; Ludwig et al., 2009). Dams and reservoirs play an important role in the control and management of water resources. Undoubtedly, mitigating floods, securing water supplies, and providing hydropower have benefited human societies in many ways, allowing for improved human health, expanded food production, and economic growth (Lehner et al., 2011).

In a regional context, the Mediterranean climate is characterized by a long dry period often extending more than 6 months (spring and summer). During this period, the water budget is negative because the potential evapotranspiration is less than the contribution of rain. In addition, the interannual variability of rainfall is very important when the rains occur in 90% in the cold season, between September and March. This precipitation can be violent up to 100 mm/h, while causing considerable runoff

(PNUE/PB, 2003). This runoff can cause diffuse erosions in water bodies and concentrated in Rivers or streams.

From an ecological perspective, the contributions of Mediterranean rivers play a key role in fertilization and productivity of adjacent coasts. Apart from the obvious hydrological changes, which mainly affect estuarine and coastal areas, the reduction in the transport of particulate material together with changes in land-use, may influence the C, N and P cycles in the river and the delivery of these elements to coastal waters (Tovar-Sánchez et al., 2016). Rivers are major pathways for transport of nutrients from terrestrial_anthropogenic sources to the Sea (UNEP/MAP/MED POL, 2013). Strong reduction in river fluxes may lead to coastal impacts such as shoreline retreat, estuarine water salinization, loss of arable lands and soil erosion, which thereby can alter the estuary topography and coastal stability (Tovar-Sánchez et al., 2016). The continuous inputs of nutrients and metals from urban and agriculture activities may lead to river eutrophication and pollution, which are considered a global threat for ecosystems, water quality, and aquatic chemistry (Cloern, 2001; Rabalais et al., 2009; Smith, 2003). Moreover, before reaching the sea, the continental origin nutrients pass the aquatic continuum of wetlands, rivers, estuaries where they undergo intense physical and chemical transformations and biological sequestration, disposal or retention (billen et al., 1991; Telesh, 2004).

River nutrients play a decisive role in the productivity and functioning of coastal waters. These biogeochemical changes are responsible for many negative impacts: loss of habitat and biodiversity, increase in the proliferation of harmful phytoplankton species, eutrophication, hypoxia (Billen et Garnier, 2007; Cloern et al., 2001; Howarth et al., 1996; Rabalais et Turner, 2001; Rabalais, 2002; Ragueneau et al., 2006; Turner et al., 2003). In the same context, (Turner et al., 2003) report that the decrease in the Si: N ratio causes severe changes in the coastal food web including fish resources.

The surface water capital in Algeria is very limited, only in the order of 12 km^3 of which 7 km^3 are being retained in dams (Figure 1). This capital is subject to strong anthropogenic pressures in particular pollution from domestic sewage, uncoordinated multisectorial use of dams (irrigation, releases, and environmental flow) and dredging of river sediments. Despite the many agencies acting in the field of water management (ANRH, ONIT, ABH, ANO, ADE) and the legislatives in particular the 0512 Law of 4 August 2005, the water resource is deteriorating, especially the decrease of water discharge into the sea. Again, Vörösmarty and Sahagian (2000) as outlined, in addition to degradation, unceasing construction of dams, irrigation of about one Million hectares of land (which assumes salinization even degradation of the quality of soils, increased evaporation, Benblidia and Thivet, 2010), the cycle of the water at basin scale is greatly changing.

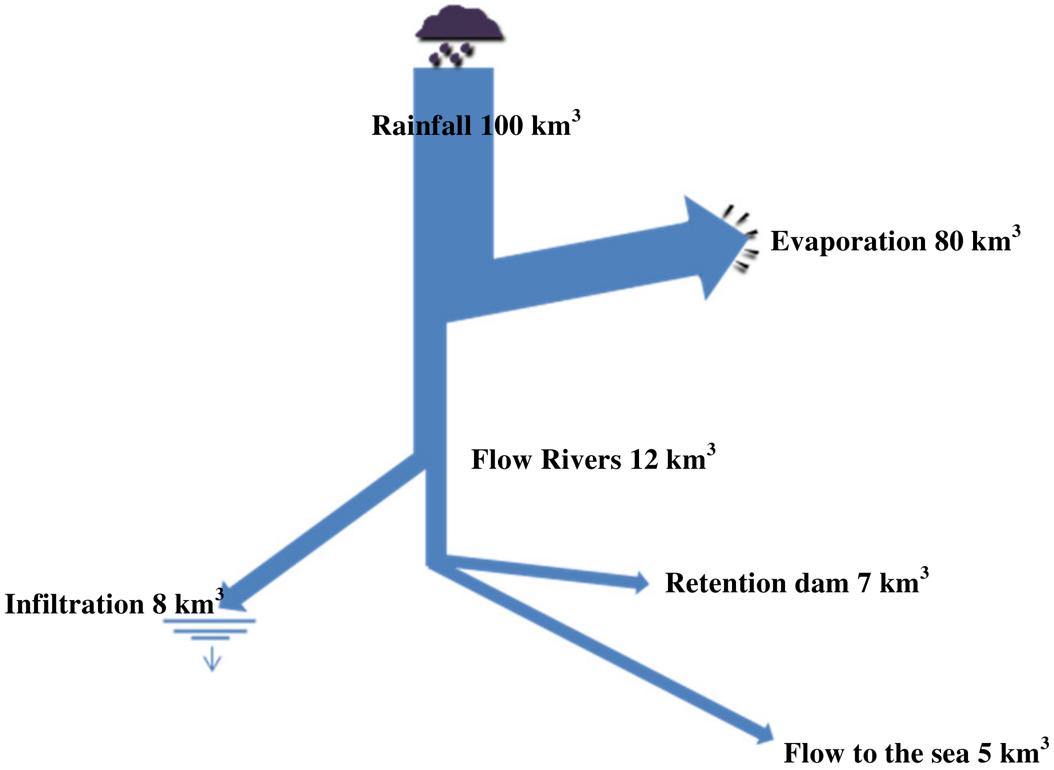

Figure 1: Water resources distribution in Algeria, according to Benblidia (2011) data. This diagram is from Bouchareb, 2013.

1.2. Impacts of human activities on the chemistry of continental waters and on the coastal waters functioning and productivity

Figure 2 depicts changes in river chemistry as a result of human activities and their implications for the biogeochemistry and functioning of coastal systems. Upstream the dams (at the upper basins) as a result of low anthropogenic inputs, water chemistry is not affected with balanced Redfield ratios (Si:N:P in the order of 106:15:1). Here, Si is more abundant than nitrogen and it is widely enough to support the needs of diatoms (Si:N ≥1). Dams have a direct effect on the retention of N, P and Si. At the downstream dams, anthropogenic releases introduce in estuaries and their mouths large masses of N and P, while the loss of Si (almost only dependent on soil wheathering) is not compensated downstream the dams. The chemistry of estuarine waters introduced to coastal waters is being altered with modified and altered Redfield ratios. The Si:N ratio often <1 causes significant impacts on the functioning and productivity of coastal waters, as shown in figure 1.

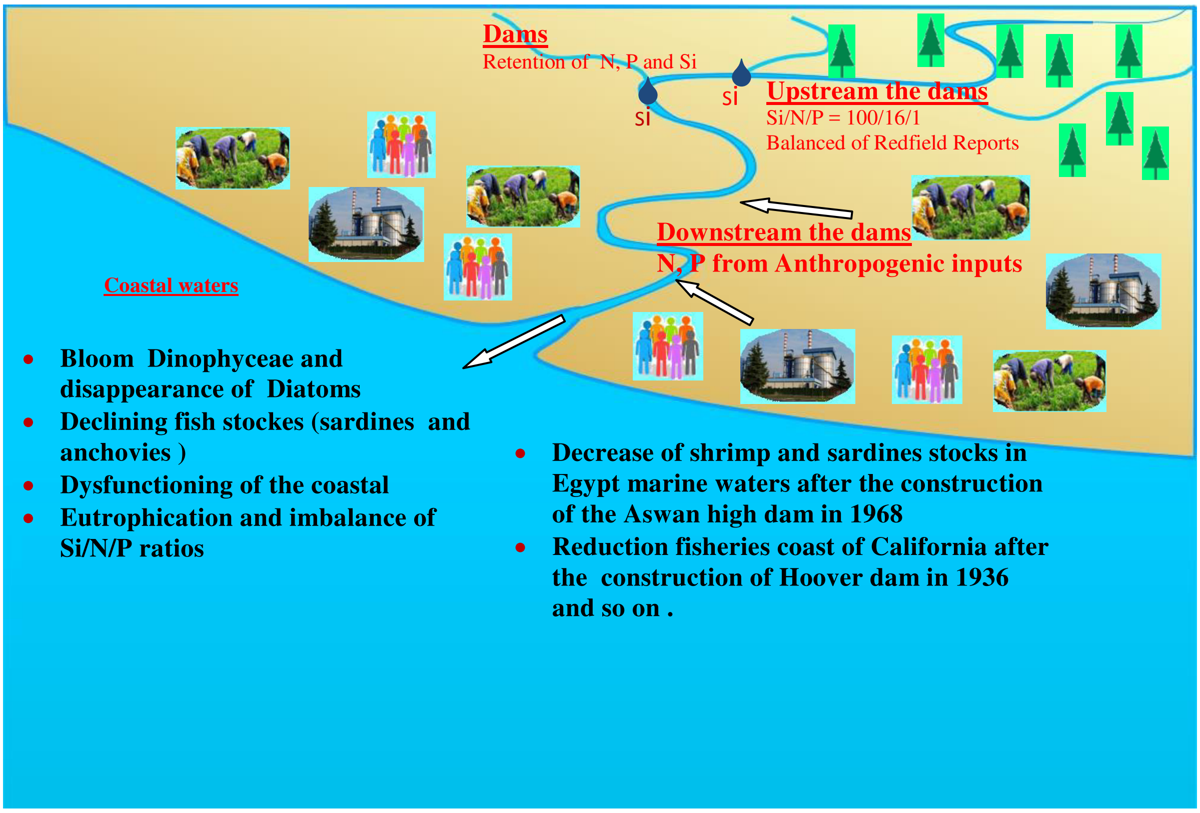

Figure 2: Diagram showing the impacts of human activities on the chemistry of continental waters and on the receiving coastal functioning and productivity. Modified from Bouchareb, 2013.

This is in particular the development of Dinophyceae phytoplanktonic species, not demanding toward Si while the abundance of diatoms decreases. The food web is affected by the decline in zooplanktonic copepods, key element in marine food webs. As a result, coastal fisheries subject to reduced continental inputs of water and Si, experiencing significant declines in landings (Wahby et Bishara, 1980; Howarth et al., 1996; Turner et al., 2003; Cloern, 2001). In Turkey, for example, the stock of anchovy, precious heritage of the nation, is lowered by a worrying manner. Similarly, the construction of the Aswan Dam on the Nile has had severe consequences for the pelagic and demersal coastal production. Wahby and Bishara (1980) reported that the landing of sardines decreased by 95% and the shrimps catch have experienced a dramatic decrease in the Nile adjacent coasts. Similarly, decreases in fish landings are reported in the California coast as a result of the construction of the Hoover Dam in 1936 (Turner et al., 2003), to cite only these examples.

1. 3. Nutrients

1.3.1. Nitrogen

Nitrogen in the aquatic environment occurs in three forms: inorganic (DIN) dissolved organic and particulate organic and detritic (or seston). DIN is formed by the ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-). Dissolved organic nitrogen (DON) is composed essentially of urea, free dissolved amino acids, complex dissolved amino acids, proteins, nucleic acids and their derivatives, enzymes and humic acids (Le Gal, 1989). In the aquatic environment, DON derived from the metabolism of micro-organisms, cell lysis, and the decomposition of organic matter and from rainwater (Meybeck, 1982). It is used by the bacteria as a nitrogen source and regenerated in mineral form (DIN) absorbed by plants. Within the DIN, ammoniacal nitrogen (NH_4) in surface waters comes mainly from agricultural and domestic waste, and to a lesser extent industrial discharges. In the low oxygen environment NH_4 dominates due to the reduction of nitrates.

Conditions of reductions and hypoxia are a sign of pollution. Nitrates often come from the nitrification of organic nitrogen, land drained by surface water, chemical fertilizers from agricultural waste, of urban, industries and farming areas. Nitrites often have low concentrations in natural waters, representing a fraction of DIN in the order of 10% (Aminot and chaussepied, 1983). Either they come from incomplete oxidation of ammonium (nitrification is not brought to completion), or a reduction of nitrate under the influence of an action or denitrifying or mineralization. The nitric and ammoniacal nitrogen in rainwater also participates to increase the quantities in surface waters. The available forms for primary producers such as phytoplankton and other photosynthetic organisms are NO_3, NH_4, but also the DON. However, ammonia is the preferred form to the phytoplankton because it is energetically less expensive and directly converted into amino acids using the glutamate dehydrogenase enzyme (Bougis, 1974). However the assimilation of NO_3 needs their conversion into NO_2 and then into NH_4 which requires the intervention of two enzymes (nitrate reductase and nitrite reductase). The nitrogen cycle has ramifications for, and important linkages with, other global cycles including that of carbon and phosphorus (Gruber and Galloway, 2008), and so the very significant present and predicted human-induced changes to this cycle have global implications. Our overall understanding of this complex N cycle is thus still developing, and following the sources, sinks, inter-conversions and cycling of this range of forms of N in estuarine and marine systems remain a formidable challenge.

1.3. 2. Phosphorus

Phosphorus is an essential element in life processes (Karl, 2000) including, photosynthesis metabolism, building of cell walls and energy transfer, and is therefore intimately associated with organisms in aquatic systems. This element is met as many forms playing a key role in the metabolism of living organisms (Monaghan and Ruttenberg, 1999): phospho-sugar, adenosine, nucleic acids (DNA and RNA), phospholipids, phosphonates, intermediate biochemical reactives (phosphocreatinine, phosphoenolpyruvate). The presence of phosphorous in water is related to the nature of the ground traversed and the decomposition of organic matter. The phosphorus present in Rivers can be divided into dissolved inorganic fraction (<0.45 microns) formed by inorganic orthophosphate and polyphosphates, and an organic fraction, in the colloidal state. The particulate fraction (≥0.45 µm) includes particulate organic and only the inorganic phosphorus directly or indirectly assimilable by the algae plays a role in the aquatic productivity. Inorganic phosphate comprises mainly orthophosphate (PO_4^{-3}) absorbed by plants.

The marine biogeochemical cycle of P differs from that of N and Si because the oxidation–reduction processes play a minor role in the reactivity and distribution of P, and the cycle is dominated by the behaviour of phosphate species. Phosphorus has however no gaseous form that has been reported at any significant concentration under normal oxygenated conditions (Gassman, 1994). In the global cycle of P (Ruttenberg, 2003) the atmosphere plays a minor role and Rivers dominate the inputs to the ocean. The majority of geochemists (Meybeck, 1982; Redfield, 1958) admit that the contributions of P from Rivers to the sea determine the level of its production. This finding is based on the fundamental difference between N and P cycle depending on the environment redox conditions. Since nitrogen is from atmospheric reservoir, any deficiency may be compensated by atmospheric fixation, unlike to the P which is a byproduct of the chemical leaching which is transported to the sea almost exclusively by Rivers (Meybeck, 1982; Froelich, 1982).

1.3.3. Silicon

Silicon (Si) is the most abundant element in the earth's crust (after oxygen) forming 28.8%; it is present in more than 370 minerals component the various rocks (Wedepohl, 1995; Wollast and McKenzie, 1983). The principal source of dissolved silica to rivers water and estuaries is from weathering of terrigenous rock minerals by naturally acidic rainwater (Drever, 1997). In estuarine and marine systems the dissolved form of silica is silicic acid $Si(OH)_4$ (Siever, 1971), whilst particulate forms are predominantly detrital quartz, aluminosilicates, opal and other Si containing minerals.

It is therefore of major interest to biogeochemists. Unlike carbon and nitrogen, its biogeochemical cycle has been little studied, probably because it was supposed to less subject to direct human disturbance and does not constitute a limiting factor with respect to its abundance in water. This element retains again the biogeochemists attention from the highlighting its major role in the control of atmospheric CO_2 consumed by planktonic algae. The dissolved silicon in water is present in different chemical forms eventually available for diatoms. The orthosilicic acid $Si(OH)_4$ (or silicates SiO_4) is the soluble form of silicon having a particularly high bioavailability. Silicates play a crucial role in the global cycling of matter particularly in the carbon cycle. It contributes doubly to the elimination of atmospheric carbon:

(1) Leaching according to the reaction:

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

Where carbon is transferred and stored in marine biogeosystems.

(2) Elimination in the seabed as diatom mud Rousseau et al. (2002) demonstrated experimentally that the diatoms are differently silicified where the Si:C ratio varies between 0.2 and 0.74. In fact, the role of the sea in the Global Carbon storage is directly coupled to the global silicon cycle, because diatoms (microscopic vegetal plankton) using Si in their shells, actually form 60% of the global phytoplankton (Tréguer et al., 1995; Ragueneau et al., 2000; Yool and Tyrrell, 2003). Diatoms absorb atmospheric CO_2

dissolved in sea water and nutrients (N, P and Si) to produce their own organic material and their envelope formed essentially of Si according to the reaction:

$$106CO_2+121H_2O+15NH_3+15SiH_4O_4+H_3PO_4 \rightarrow 106\ (CH_2O)\ 15(NH_3)15\ Si(OH)_4H_3PO_4$$

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

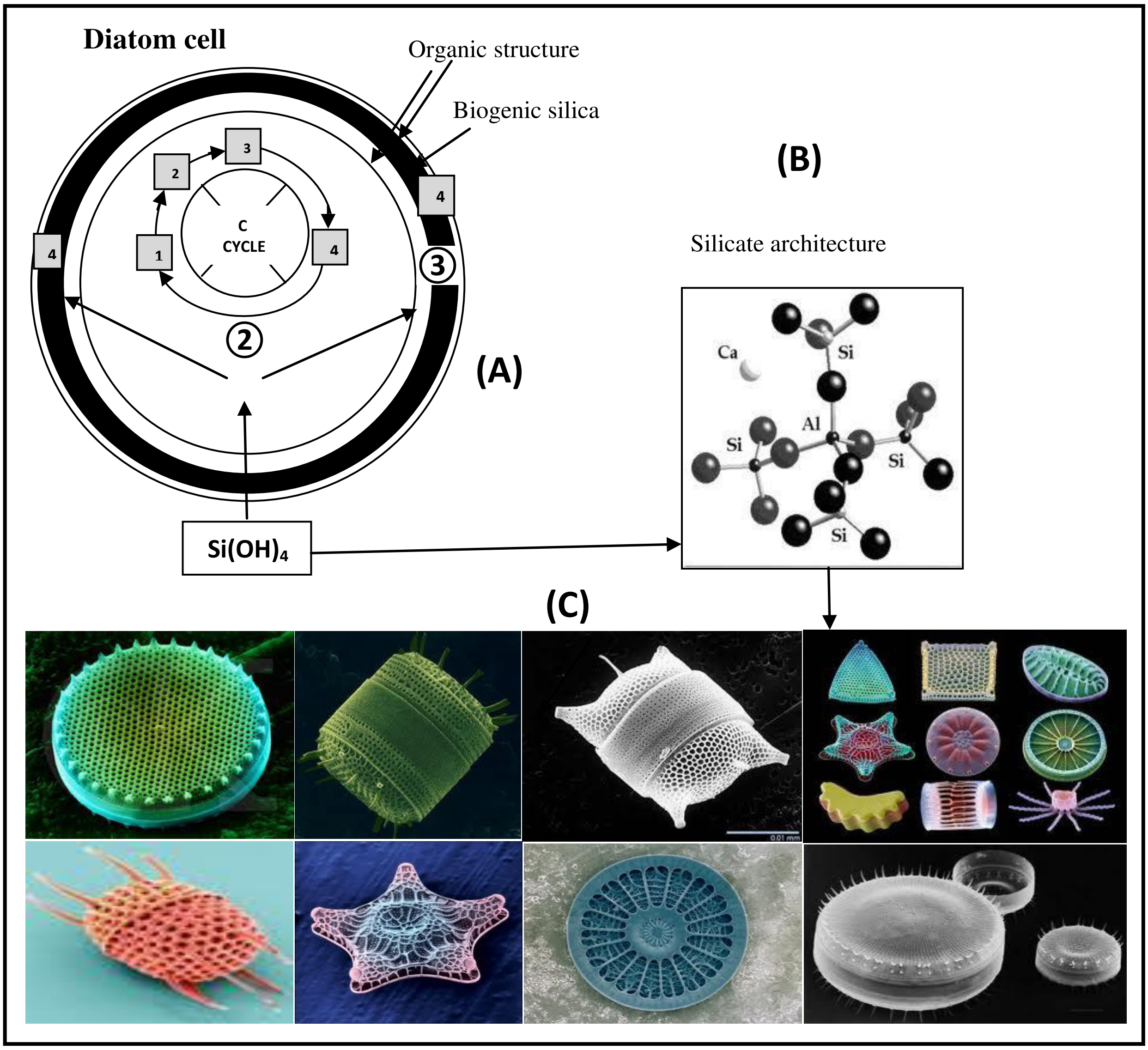

Figure 3: A: absorption of silicon in the form of silicates [$Si(OH)_4$] by the diatom cell during its growth ❶: absorption of $Si(OH)_4$ or $Si(OH)_3$, Na + and co-transporter, ❷: assimilation,❸: building envelope by polycondensation ❹Growth and deposition If belts, bands or thorns S: DNA replication, G1 & G2: intermediate phases; M: mitosis; B: architecture silicates; C: Sample forms of siliceous envelopes of diatoms over and modified Heip, C., and Middelburg, J., Netherlands Institute of Ecology, Yerseke. From Bouchareb, 2013.

1.4. Particulate organic matter

The organic matter present in the water is generally divided into two fractions: the dissolved organic and particulate organic matter. The usual definition of particulate organic matter (POM) based on the operation of filtration that allows isolating. POM covers the field of all the particles, active or inert, organic carbon representative and whose size is greater than 0.45 µm (Figure 3) (Gourlay, 2005). The particulate organic matter in aquatic environments is formed by the set of suspended solids that are not completely mineral. These include, for example organic polymers colloids, bacteria, and the entire phytoplankton (Figure 3).

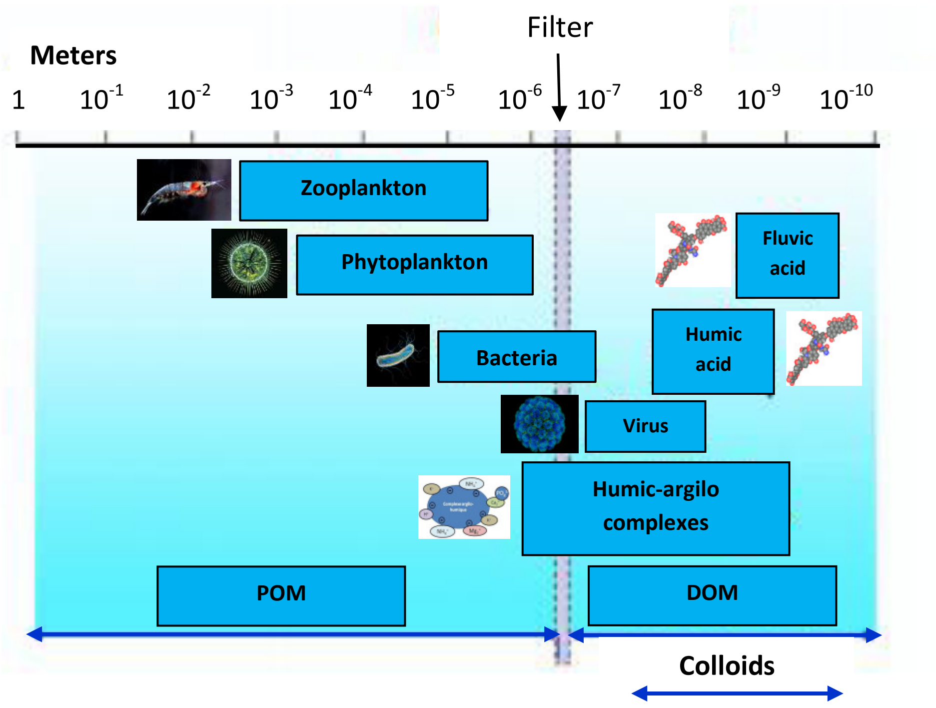

Figure 4: Size spectrum of dissolved and particulate organic matter. DOM: dissolved organic matter; POM: particulate organic matter. From Pellet (2005).

The POM binding capacity for organic micropollutants is an increasing function of their hydrophobicity (Schwarzenbach, Gschwend et al. 1993).

1.4.1. Particulate organic carbon (POC)

There are four different forms of carbon in River systems (Garrels and Mackenzie, 1971; Al Droubi et al, 1976; Meybeck, 1993; Amiotte Suchet, 1995; Meybeck et al., 2005): dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate inorganic carbon (CIP) and particulate organic carbon (POC). For DOC and POC , they come mainly from three sources (Meybeck, 1983; Meybeck et al., 2005): (i) organic carbon allochthonous "natural" in the particulate or dissolved form, such as humic material from the soil of catchments ; (ii) the native organic carbon that comes from the primary production of the aquatic environment such as higher plants (macrophytes), benthic algae and phytoplankton; ; (iii) allochthonousorganic anthropogeniccarbon (domestic waste, industrial and agricultural processed or unprocessed), a phenomenon termed "organic pollution". Furthermore, there are two sources for the POC: Organic carbon from the mechanical erosion of soil (soil POC) and organic carbon from the mechanical erosion of rocks (litho POC); (Meybeck, 1993; Ludwig, 1998 Meybeck et al., 2005). Carbon bonded to molecules having a size above the filter cut-off used to separate the filtrate of the particulate phase (usually> 0.22 µm and 0.45µm) (Petit Jean et al., 2004). Good correlations were observed between the fluxes of POC and rates of erosion and lesser but significant correlations between flow in and fluxes in POC (Meybeck, 1993; Ludwig, 1998; Meybeck et al., 2005). The POC concentrations (mg/L) significantly increase with flow and TSS concentrations, the maximum POC may precede the peak flow (Meybeck 1993; Meybeck et al., 2005).

1.4.2. Biogenic silica (BSi)

Biogenic silica corresponds to the particulate silica fraction derived from organism's growth and cycling. Yet the silica is the most abundant chemical compound of the Earth's crust (Vrieling et al., 2003). Silica provides many functions in natural systems: from protists to higher plants this silica performs the functions of support and protection (Figure, 3). In the marine environment, silicification by external frustule concerns in particular the phytoplanktonic diatom populations, and siliceous endoskeleton is specific to silicoflagelles and Radiolarians. According to Mortlock and Froelich (1989), the general formula of biogenic silica is SiO_2, 0.4 H_2O.

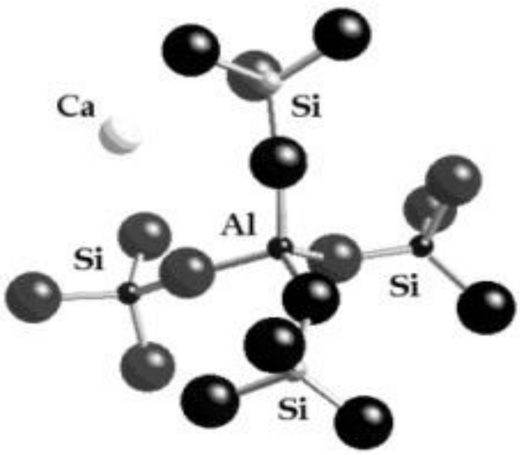

Figure 5: structural model of biogenic silica. Al enters the network structure while preserving the three-dimensional environment from sharing SiO_4 tetrahedra. The substitution of Si^{4+} by Al^{3+} generates the other a negative charge. Chemical analysis of the composition of diatom frustule suggests load compensation by Ca^{2+} ions (Gehlen et al., 2002).

Diatoms play a major role in primary ocean production and are also an important component of the export of organic carbon to the deep ocean. The study of the factors governing the contribution of diatoms to production is an important element in understanding the mechanisms of controlling the effectiveness of the biological pump in several regions of the ocean. The reconstruction of past fluxes for the export biogenic silica is also crucial to trace the past fluxes for the export of organic carbon to the deep ocean as well as the C_{org} /C_{carb} ratio of sedimentary material, which are two important factors in the control of TCO_2 and the alkalinity of surface waters and thus the atmospheric TO_2 (Quéguiner, 2013).

1.5. Total suspended solids (TSS)

The solids in rivers are in dissolved form (TDS) and suspension (TSS). The TSS is retained in the filter while the TDS pass there through. The TSS includes a wide variety of materials: sediments, plankton, plant detritus and animals and domestic and industrial waste. In rivers, dams or coastal areas, The TSS act as modulators of the transported materials (pollutants, nutrients) in dissolved or particulate form. They regulate the transparency of the water, the depth of the photic zone and thus regulate primary and secondary production. They also regulate the production of bacterio plankton (which it is attached), and therefore influences the mineralization and consumption of the oxygen content (Håkanson, 2006). Several factors are known to influence the TSS in aquatic environment (bouillon, 1994, 1997; Wetzel, 2001) which are the most important autochthonous production (plankton and its excrement), allochthonous materials of atmospheric origin and resuspension of the materials.

The allochthonous materials of atmospheric origin and resuspension of the materials. In addition, the TSS in rivers also reflects the significant erosion of drained land and soil fertility. The erosion is a transfer of material (material removal), and sometimes fertility from one place to another. The impacts are of different natures, one hand on the spot where erosion and also occurs in the places where these materials have accumulated. The erosion due to runoff has serious threat to deriving their Mediterranean soils (UNEP/PB, 2003). When the action of the water is concentrated in the ravines and rivers, sediment load is large (5 to 130 g L^{-1}) and erosion becomes significant (Roose, 1991). The fertility of soil is both its fertility in salts, biological and physical. It expresses the ability of the soil also provide a good anchor, water and oxygen to the plant roots; It depends on its texture, its structure, its composition, its permeability, porosity, its depth, its capacity of water (Roose, 1991). When some chemical elements are leached and exported, this causes a depletion of soil salts (N, P, K in particular) or conversely, become excessive leading to salinization, acidification, eutrophication and pollution by toxic substances. UNEP/PB (2003) reported a loss of 12-15 t/ha/yr of soil sediment exceeds the average speed of rocks alteration and then unbalances the morphogenesis and pedogenesis.

1.6. Total dissolved solids (TDS)

The dissolved solids or total dissolved solids (TDS) are by definition the mineral salts, organic matter and other substances dissolved in water (US/EPA, 2001). In literature, very often the TDS are assimilated or confused with the salinity of the water. In fresh water, the TDS include soluble salts such as Na^+, Ca^{2+}, K^+, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-, SiO_2, PO_4^{3-}, NO_3. They include solids which may pass a filter of porosity 0.45 µm and hence measure the amount of substances dissolved in water. According to Wetzel (1983) fresh water has a TDS content of less than 1000 mg L^{-1}. TDS are sometimes used as a "watchdog" in the quality monitoring of the aquatic environment. Any change in the ionic composition between the test sites in the river can be quickly detected by the conductivity meter. The electrical conductivity relationship (EC) and TDS strongly varies according to the river: TDS = 0.4 to 0.93 EC. By default, the conductivity is designed to convert a unit of EC in ½ units of TDS. However, it is just an approximation as the conversion factor varies from simple to double water (0.4 to 0.9). Indeed, in addition to the geological nature of leached soils, the load of rainwater, irrigation water (loaded with fertilizers) that returns to rivers, domestic waste may change the composition and the TDS content of the river waters. The global average concentration of TDS in river water is 120 mg L^{-1} according to Wetzel (1983).

CHAPTER II

Kebir branch (kebir Rhumel)

CHAPTER II: MATERIALS AND METHODS

1. Presentation of catchments

The three studied catchments streams have a total area of 11170 km^2 with a population density over three million. They are primarily subject to diffuse domestic and agricultural discharges (Figure 6) and strongly intercepted by dams that hold more than half of the capital flow.

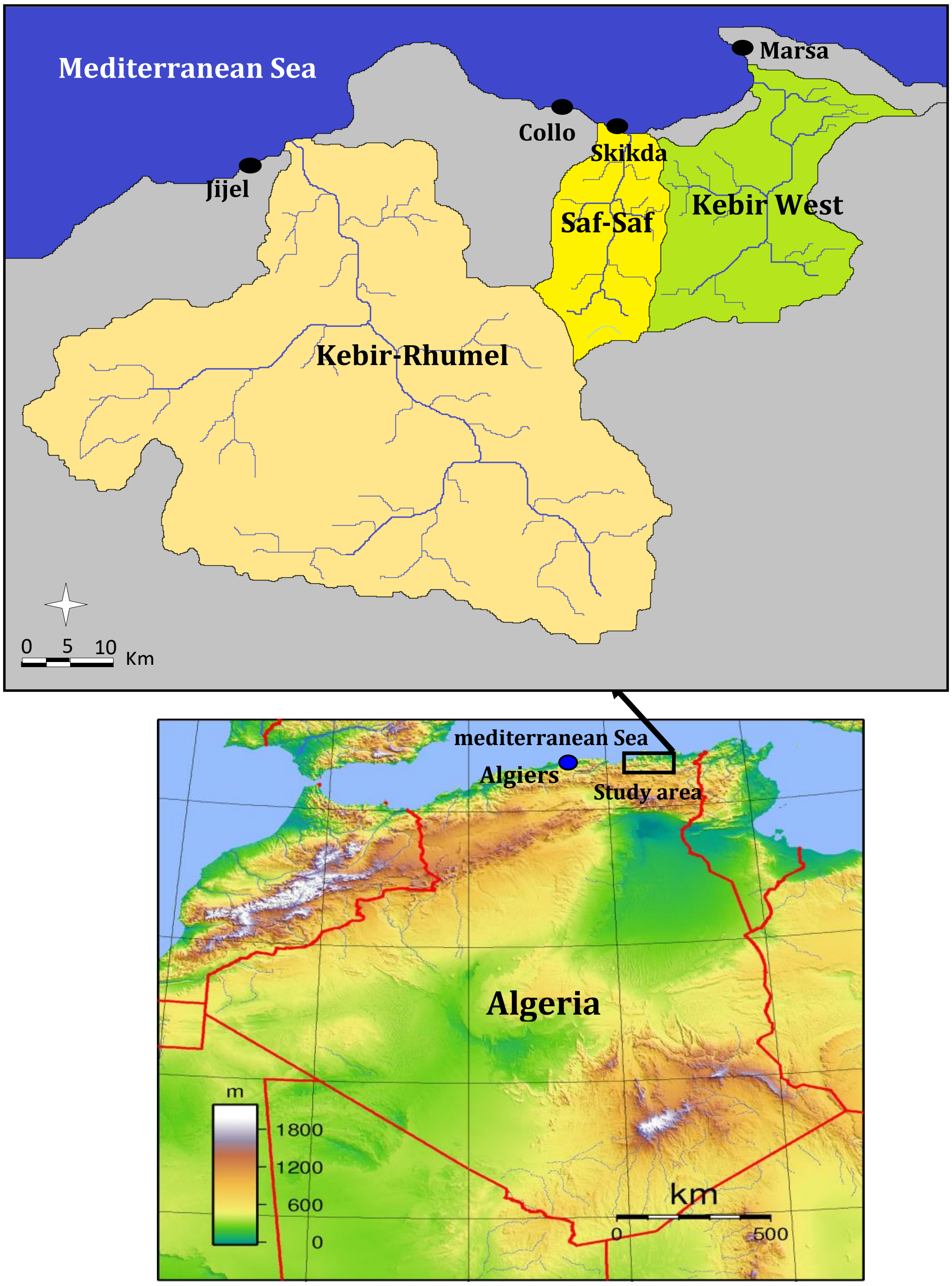

Figure 6: Map showing the studied catchments (Kebir-Rhumel, Kebir West and Saf-Saf).

1.1 Kebir-Rhumel catchment

The catchment of the Kebir-Rhumel stream having an surface area of about 8110 km² (ABH, 1999), covers the northern margins high plateaus south of Constantine, the Mediterranean Sea to the north, the basin of the Seybouse to the east and the basin of the Soummam west (Figure 7). Kebir-Rhumel catchment comprises the two permanent streams the Rhumel and the Kebir, which drain an area of 5315 km² and 2160 km², respectively. The climate varies slightly from North to South, passing from a sub-humid area to a semi-arid area. Generally here the Mediterranean climate prevails which is humid and temperate, characterized by a mild winter and hot summer, with some rich water resources of different origin (rain, hail snow). Usually the snow made its appearance on the massifs of high altitudes. Precipitation is the essential factor who governs the flow of watercourses. Indeed, they have a direct effect on the water flow. The average precipitation in the Kebir-Rhumel catchment is estimated about 506 mm according to management data from Beni-Haroun dam in 2012.

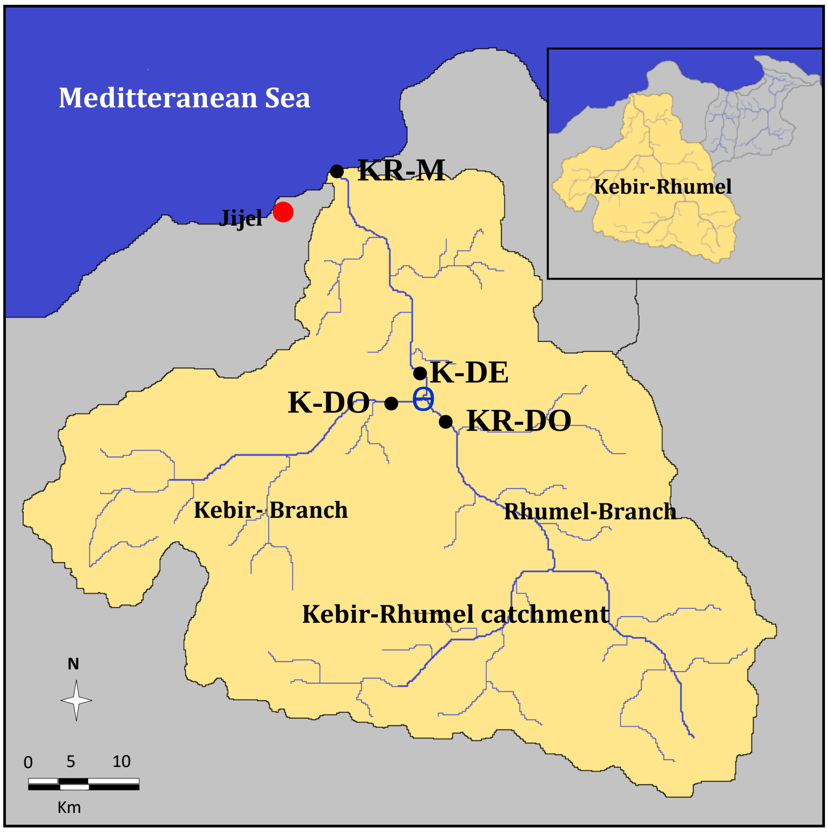

Figure 7: Map showing the studied stations in Kebir-Rhumel catchment: **ϴ**; dam; R-DO: entrance of Rhumel branch in Beni-Haroun dam; K-DO: entrance of the Kebir branch in Beni-Haroun dam; KR-E: exit dam station (confluence); KR-M: mouth of Kebir-Rhumel stream.

The Kebir-Rhumel waters contain a mixture of domestic, industrials, agricoles and atmospheric deposition water supplies. Kebir-Rhumel catchment is characterized by a mixed traditional (gravity irrigation) and intensive (irrigation by spray canals and fertization) farming. The currently irrigated area in the catchment is estimated to reach around 30000 ha, which uses 27.65 million m^3 of Beni-Haroun reservoir water. The main activities of the irrigated areas are essentially vegetable crops and arboriculture. The most commontly fertilizers used in agriculture are ammo-nitrate (NH_4-NO_3 33%) and superphosphate (45%). The industrial fabric is primarily concentrated around the large towns (Constantine, El Khroub, Chelghoum Laid, Hamma Bouziane, and Mila).

In Kebir-Rhumel catchment, Beni-Haroun dam was built in 2005 to intercept runoff from the two main branches Rhumel and Kebir. The dam was only operated from 2007, mainly for the consumption of the population and irrigation. Beni-Haroun is the largest dam in Algeria with 118 m depth, and a storage capacity of 960 million m^3. This great dam includes a pumping station with a total capacity of 180 megawatts, located 50 km to the Northwest of Constantine and 100 km from Jijel. This station delivers 22.5 m^3/s up to an expansion tank located at a height of 880 m transferring water to the dam of Oued Athmenia (20 million m^3), will be directly fed the cities of Constantine, El Khroub, Ain Smara, Chelghoum Laïd of Oued Athmania, Oued Seguin and Telerghma. The flow of the Rhumel branch (Figure 7) is more important than Kebir, but it is highly subject to the discharge of untreated sewage from the cities of Constantine and Mila in addition to many other contigous agglomerations. The sub-watershed of Kebir is sparsely populated and less forested from the Rhumel branch. In 2012, the water residence reached 8 months, but was very weakly renewed during 2010 (43 months) (Ounissi and Bouchareb, 2013)

Figure 8: photos of the different studied stations for Kebir-Rhumel catchment and Beni- Haroun dam.

1.2 Kebir West catchment

The Kebir West stream is a coastal region Northeast Algerian part of the great Constantine basin. It occupies an area of about 1900 km^2, characterized by a dense river network. It includes two streams, oued Kebir West and oued Magroun. Kebir stream is the largest of them, both in length and speed. Eight other streams that drain El Marsa coasts (Figure 9).

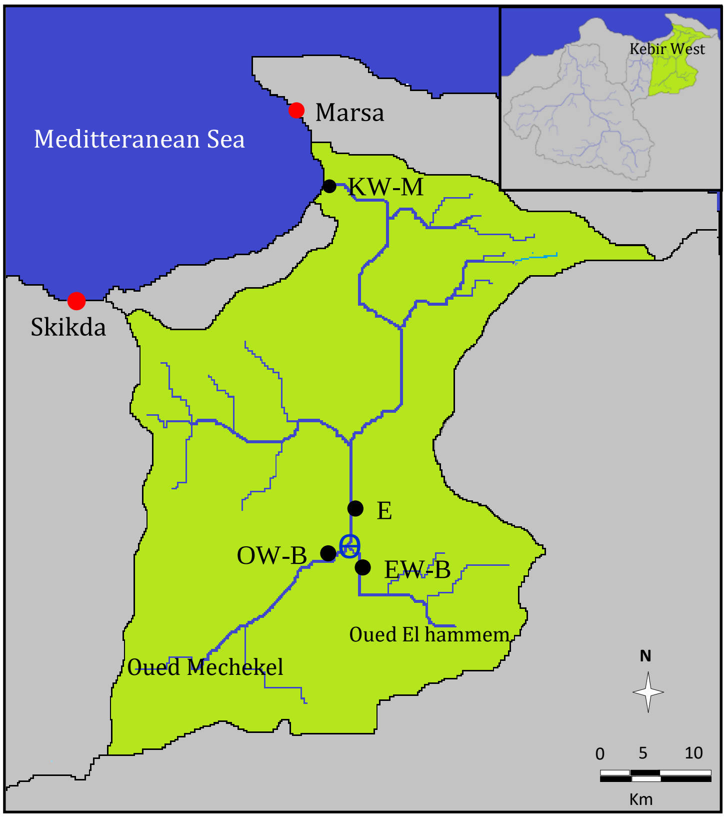

Figure 9: Map showing the studied stations in Kebir West catchment (KW): **ϴ**: Dam; OW-B: western entrance Zit Amba dam; EW-B: eastern entrance Zit Amba Dam; E: Exit Zit Amba Dam stations; KW-M: mouth of Kebir West stream.

The geographical features and Mediterranean climate have allowed the installation of favorable conditions to the storage of an important water reserve. The Smahdja wetland is habitat of great importance, sharing numerous wildlife types and different species of flora. The average precipitation over the Kebir west stream is estimated between 800-900 mm (Marre, 1992). Titi Benrabah et al. reported a precipitation yield of 664 mm and 100.5 mm as height discharge (about 18 m^3 s^{-1}) for 2010. Agricultural land occupied by crops in the Kebir stream include the cereacultures, fallow land, agroalimentary crops especially tomatoes. They occupy an area of 170 km^2, or almost half of the total area of the sub stream which indicates the agricultural vocation of the area. These lands are located primarily along the river. The industrial factory in the Kebir West stream is limited to two plants: Tomatoes plant at Ben Azzouz and the strong cement plant at Bekkouche Lakhdar which daily require large amount of water.

The Kebir West catchement is weakly populated, with only 30 inhab/km^2 and it is managed by Zit Amba dam (120 million m^3 storage capacity). Zit Amba dam is fed by tow tributaries of Kebir West stream, with Oued El hammam on the South and Oued El hammam on the West. Oued El hammam is submitted to some urban pollution sources and hydrothermal wastewater, but Oued Mechekel delivers however more clean waters. By summertime, the two branches fall almost dry at their entrances into Zit Amba dam. The exit of Zit Amba dam extruded, however, low water amounts that entertain some agricultural and the stream environmental services. The water residence time (storage capacity/discharge (Rueda et al., 2006) of the studied dam is largely variable according to the stream input, storage capacities and clogging rates. In 2012, the water residence reached 4 months, but was very weakly renewed during 2010 (28 months) (Ounissi and bouchareb, 2013).

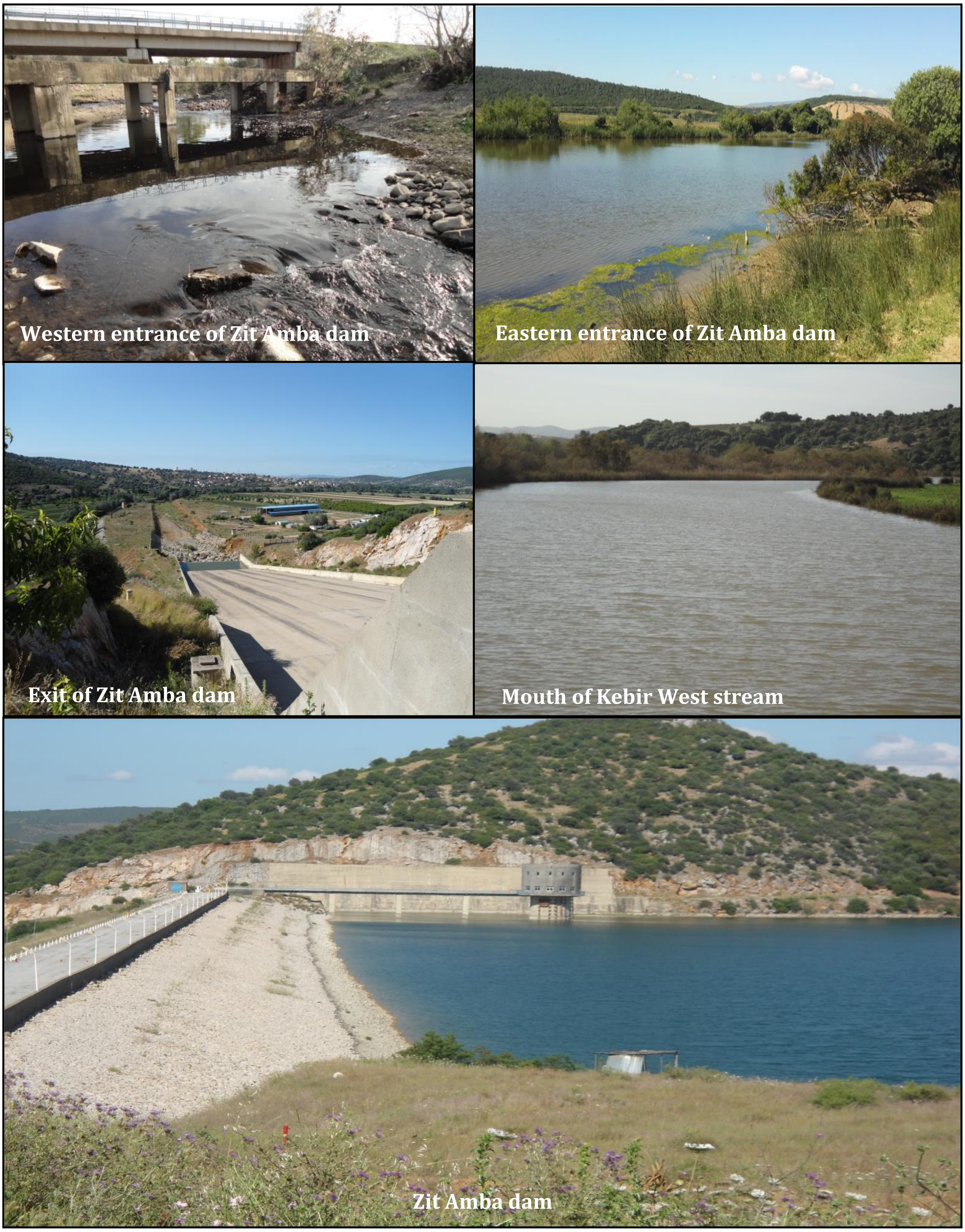

Figure 10: photos of the different studied stations for Kebir West stream and Zit Amba dam.

1.3. Saf-Saf catchment

The Saf-Saf catchment belongs to the coastal basin of Constantine and lies between the catchment of the oued Guebli in the West and that of oued Kabir West to East (Figure 12). It is limited to the south by Djebel El Hadjar and Jebel Oucheni, to the east by Jebel El Alia and Tamgout, to the west by the mountains of Jebel Boukhallouf and Collo, and the Mediterranean Sea to the north where pours the main stream in this catchment to the east of Skikda city. The catchment draining an area of 1158 km^2 (Figure 12).

The precipitation reached 672 mm yr^{-1} according to the weathering station data during the year of 2012 (Figure 11) over the whole catchment but the mobilized amount is reduced to over 50 million m^3 yr^{-1}. The population of Saf-Saf catchment is around 500000 inhabitants. The Zerdaza dam is fed by Saf-Saf, which permanently flow unlike the eastern streams that are temporary and not frankly flow during the floods.

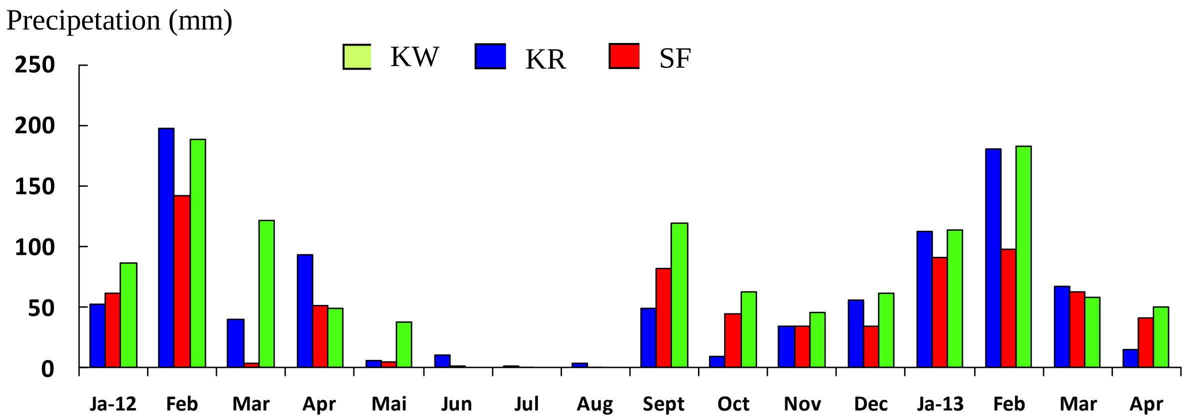

Figure 11: monthly precipitation (mm) in three studied catchments (Kebir-Rhumel, Kebir West and Saf-Saf) during the study period.

The dam was built between 1929 and 1945 and raised in 1974 (ANBT). It is used for drinking water supply of several villages as well as Skikda city and its industrial zone. The storage capacity of the dam is 32 million m^3, and around 18 million m^3 is the regularized volume. The excessive inputs of sediments have greatly reduced the initial storage capacity. Therefore, the water layer was substantially decreased and the residence time of water was then limited to a few weeks. However, the upper part of the Saf-Saf catchment is largely forested while the lower part is mainly occupied by agricultural land. By summertime all streams fall almost dry at the entrance of dam, while the exit of the dam continues to provide low flow. The low catchment supports large intensive agricultural activities and the land use is mainly dominated by agricultural land and the forest generally occupies less than 15%.

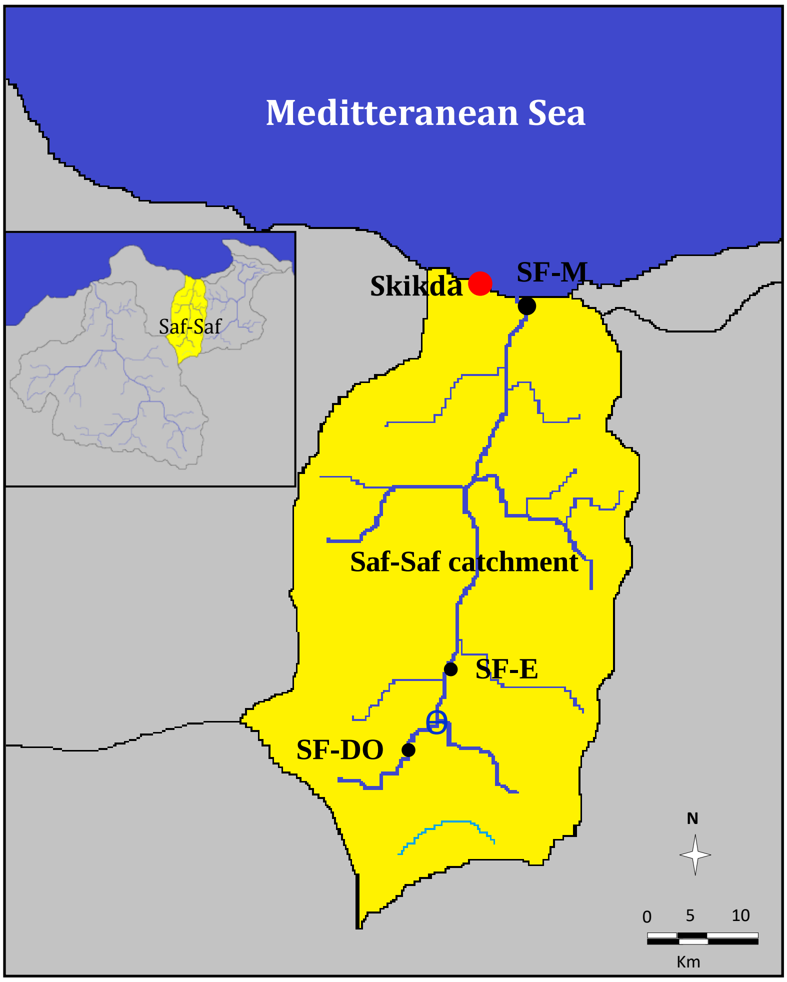

Figure 12: Map showing the studied stations of the Saf-Saf catchment (SF); **ϴ** : Dam; SF-DO: entrance SF dam; SF-E: dam exit ; SF-M: Saf-Saf stream's mouth.

Figure 13: photos of the different studied stations for Saf-Saf catchment and Zerdaza dam.

2. Methods of hydrological and biogeochemical analyses

2.1. Hydrological data

The hydrological parameters and the different nutrients were sampled twice a month from January 2012 to April 2013 in three stations in the Saf-Saf catchment and four stations for each of the catchments Kebir-Rhumel and Kebir West (Figures 7, 9 and 12, Table 1) . However, the catchment of KR was sampled from the entrance of the Rhumel branch and Kebir branch as for KW catchment from the entrance of Oued Mechekel and Oued El hammem (Figure 7 and 9).

Table 1: location (latitude, longitude) of the studied stations of different catchments.

Catchment	Name	Location
Kebir-Rhumel	KR	
Rhumel at the entrance of Beni- Haroun dam	R-DO	N36°35'04.53' E6°16'35.01'
Kebir at the entrance of Beni-Haroun dam	K-DO	N36°45'4380' E6°15'.15.24'
Kebir-Rhumel at the exit of Beni-Haroun dam	KR-DE	N36°50'21.29' E6°06'54.39'
The mouth of Kebir-Rhumel stream	KR-M	N36°29'45 .51' E6°06'14 .48'
Kebir West	KW	
Oued El-Mechekel the entrance of Zit Amba	OW-B	N36°41'41.02'E7° 19'33.88'
Oued El-Hammem the entrance of Zit Amba	EW-B	N36°41'57.98'E 7°18'38.14'
Kebir West at the exit of Zit Amba dam	KW-DE	N36°38'12.90'E 7°20'14.74'
The mouth of Kebir West Stream	KW-M	N 36°57'10.79 E7°15'39.55'
Saf-Saf	SF	
Saf-Saf at the entrance of Zerdaza dam	SF-DE	N36°35'30.90 E 6°53'54.90
Saf-Saf at the exit of Zerdaza dam	SF-DO	N36°33'55.90 E 6°56'00.43
The mouth of Saf-Saf stream	SF-M	N36°51'32.94 E 6°56'14.94

This purposive sampling strategy allows understanding changes materials levels along with the river system and the receiving coastal. This facilitates the monitoring of nutrients and physical parameters across the entrances, exits and stream mouths. This purposive sampling represents a Eulérien monitoring of water chemistry. Although it is an economist strategy maximizing the information regarding the sampling effort, it provides the average of the different estimators (across the entire basin), but it is unfortunately not representative (Sherrer, 1984). Indeed, the stations have been structured in order to identify spatial trends or gradient, and whatsoever the estimator is subject to bias (including correlations, mean, etc.).

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

Two liters of water from the middle of the flow were collected for nutrient analysis of nutrients and particulate organic matter (POC and BSi). The water samples for analysis of the nutrients and particulate organic Carbone are placed in glass vials except for the silicon and biogenic silica which necessitated the use of polyethylene bottles. The filtration of samples is made the day of sampling and chemical analysis is done in the following two days.

2.2 Evaluation of nutrient flux, salts (TDS) and total suspended solids (TSS)

The instantaneous fluxes of nutrients were calculated by multiplying their concentrations by the river flow. The annual loads of 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/year or t yr^{-1}), Ci is the concentration of nutrients (µmol l^{-1} or 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.

Nutrient fluxes, total solids suspended and total dissolved solids to and from the dams were also calculated in order to evaluate their budgets to from retention rates or production. Estimates of fluxes from upstream and downstream of dams were started only in January 2012; and the calculations were made for the period January 2012-December 2012. However, in the Mediterranean diet the flow is maximum during wet periods, which suggests that the estimation of nutrient fluxes will be underestimated. Moreover, the flux entering the Beni- Haroun dam represents the sum of the Rhumel and Kebir branches. The same of Zit Amba dam represents the sum of Eastern and Western branches.

Retention (R%) of nutrients, TSS and TDS were calculated as follows:

$$\mathbf{R\,\% = 1 - (E\text{-}S) / E.\ 100}$$

Where E is the content at the entrance of the dam and S the content at the exit of the dam. The negative value indicates retention or elimination in the dam and the positive value denotes rather a production by the dam.

2.3 biogeochemical analysis methods

In the laboratory, water samples collected for dissolved nutrient analyses were filtered through Whatman GF/C glass filters (0.5-µm porosity). The dissolved nutrients were analysed on the same or the following day. For silicates (SiO_4 or orthosilicic acid [$Si(OH)_4$] and particulate biogenic silica (BSi) determination, a fraction of each sample was filtered through polycarbonate filters. Particulate matter was stored at -20°C for one day and analyzed. The dissolved inorganic nitrogen DIN (ammonia: NH_4; nitrate: NO_3; nitrite: NO_2), dissolved organic nitrogen (DON), phosphate (PO_4)and SiO_4 were determined by means of standard colorimetric methods described in Parsons et al. (1989). The total dissolved phosphorus (TDP) and polyphosphate (P_2O_5) were measured following the standard method of Rodier (1996). Dissolved organic phosphorus (DOP) was obtained by subtracting the dissolved inorganic phosphorus (DIP = PO_4 + P_2O_5) from TDP. Total Suspended Solids (TSS) was measured using two water subsamples of 250-500 ml (depending on the water sample turbidity), following the method described in Parsons et al. (1989).

Particulate organic carbon (POC) was determined following the method of Le Corre (Aminot et Chaussepied, 1983). Two fractions have been distinguished; the fraction <200 µm (mainly phytoplankton particles) and the fraction >200 µm (mainly zooplankton particles). The filtered volume and filters are the same as those used for TSS. Biogenic particulate silica (BSi) was determined according to the method of Ragueneau and Tréguer (1994). The particulate biogenic silica retained on polycarbonate filters was digested to extract the corresponding $Si(OH)_4$. $Si(OH)_4$ level was analyzed by the standard colorimetric method described in Parsons et al. (1989).

Table 2: Summary of analytical methods (**1**: Parsons et al. (1989); **2**: Rodier (1996).

Element	**Methods**	**References**
Ammonia nitrogen (NH_4^+ + NH_3^+) or NH_4	Spectrophotometric analysis; λ = 630 nm	1
Nitrites (NO_2^-) or NO_2	Spectrophotometric analysis; λ = 543 nm	1
Nitrates (NO_3^-) or NO_3	Reduction of NO_3^- to NO_2^- ; Spectrophotometric analysis; λ = 543 nm)	1
Dissolved organic nitrogen (DON)	Mineralization in basic medium and indirect Spectrophotometric analysis in the equivalent of NO_3 , at NO_3^- ; λ = 543 nm	1
Phosphate (PO_4^{3-})	Spectrophotometric analysis; λ = 885 nm	1
Polyphosphate (P_2O_5)	Spectrophotometric analysis; λ = 885 nm	2
Total dissolved phosphorus (TDP)	Spectrophotometric analysis; λ = 885 nm	2
Dissolved organic phosphorus (DOP)	Decuced from the difference TDP et DIP : DOP = TDP- (PO_4 + P_2O_5)	2
Orthosilicic acid [$Si(OH)_4$] ou SiO_4	Spectrophotometric analysis; λ = 810 nm	1
Total suspended solids (TSS)	differential weighing	1

- **Sampling of biogenic silica**

The recommended protocol for the analysis of amorphous silica (I.e biogenic) in oceanic waters of the southern is derived from the hot sodium hydroxide digestion method of Paasche (1973). It has been detailed by Brzezinski and Nelson (1989), used succefully in different offshore provinces of the world ocean (e.g Brzezinski and Nelson 1989, Treguer et al., 1990) and refined further since that time. Note that only high quality reagents with very low-Si content are to be used along with Si-free deionized water (DIW). To minimize silica concentration from glass, polyethylene or poly carbonate wares must be used for samples and reagents.

1. Collect either 1 liter (photic zone) or 2.5 liters (subsurface and deep waters) of seawater. Filter under a vaccum of about 60 mm Hg through a 47 mm polycarbonate membrane filter (0.4 um por size) using plastic filter tower.
2. Fold the filter in quarters, place it in a plastic petri dish (it must fit loosely) and dry at least 12 h at 60°c.store under dry conditions in closed plastic petri dish until the analysis is performed.
Biogenic silica (BSi) determination:

1. Place the filter in the bottom of a 15 ml conical centrifuge tube made of polymethyl penten (PMP). Add 4.0 ml of 0.2 N NaOH in DIW. Digest in a water bath at 95°c for 45 minutes (the cap must not be on tight during this digestion time).
2. Transfer the tube to an ice-water bath. When cool add 1 ml of 1.0 NHCL in DIW. Shack well.
3. Using a stainless or plastic stapula, jam the filter into a tight wad in the bottom of the PMP tube. Centrifuge for 5 min at 1500 x g to separate the remaining suspended materiel (to be analysed for lithogenic silica determination) supernatant.
4. Withdraw 4.0 ml of supernatant using a plastic volumetric pipette. Dilute to a total of 10.00 ml with DIW in a 50 ml polypropylene centrifuge tube (extra dilutions could be necessary for high BSi concentration). Analyse by either a manual or automated acid/molybdat colorimetric method (from standard curve in DIW, using dried Na_2SiF_2 the standard.
5. Calculate the BSi concentration (in $nmol.l^{-1}$)of the original seawater sample by Eq.(I):
   Eq. (1): BSi=12.5*(Si $(OH)_4$) represents the silicic acid concentration measured in the 10.0 ml sample (in µM) and V_f the volume of seawater filtered (in liters).
   Blanks are determined by performing the digestion and subsequent analysis on virgin poly carbonate membrane filters. The blank should be equivalent to <10 nmole-Sil^{-1}.

❖ Sampling of particulate organic Carbone

The method of Lee (Le Corre, 1983) described in the manual Edition in the manual of Aminot et Chaussepied (1983) allows evaluating the material organic particulate in the water in the form of carbon equivalent. Organic matter collected on a glass fibre filter is oxidized by mixture sulfochromique. Oxidant in excess is dosed in return by a solution of Fe (II).

- **The pre-filtration**

To consider the phytoplankton particles the sampled water was first pre-filtered by using a sieve of 200 µm mesh opening. This POC fraction <200 µm is assumed to mainly comprise the phytoplankton organisms (living and debrits), and named POC1. The remaining fraction (>200 µm) is also considered to be analyzed as zooplankton carbon particles, and named POC2. POC1 +

POC2 is the total POC (POCt).The mesh is the same for all samples of material particle performed simultaneously. At the pre-filtration, action is implemented by the following procedure:

-Homogenize the sample.

-Place the screen and the center of the beaker.

-Measure as soon as the volume: to be representative must be equal to 250 ml.

-Pour the sample on the sieve and then gradually filter all the measured volume.

-Make Siever insing with distilled water.

Calibration is made from glucose solution. Thus obtained glucose carbon equivalent (Aminot and Chaussepied, 1983).

- **Filtration**

Filtration is performed on filters, Whatman GFC of 4.7 cm in diameter, prior to the oven racks to maximally eliminate all organic traces.

During filtration, the following procedure is implemented:

Equip the slide of a treated filter filtration as indicate above. Operate with own metal tongs and immune particle air (dust, smoke).

Homogenize the sample. Filter the water out from under reduced pressure: do not go below 0.5 bar. What risk of break up particles and phytoplankton cells. After leaving the filter come to sec.

➢ **Reagents:** (Aminot et Chaussepied, 1983)

✓ **Oxidant mixture**

Dissolve 4.84 g of potassium dichromate $K_2Cr_2O_7$ in 200 ml of distilled water, add little by little solution to 500 ml of concentrated sulfuric acid H_2SO_4.

✓ **Normal solution of Fe (II) 0.1**

Dissolve 39.21 g double sulfate of iron and ammonium (mohr's salt) in 1/2 l water distilled, add 20 ml of sulphuric acid H2SO4 and make up to 1000 ml with distilled water.

✓ **Glucose Solution**

Dissolve 7.5 g of glucose $C_6H_{12}O_6$ in distilled water and make up to 100 ml.

Operating mode

The filtration is done on filters, Whatman (GF/C) 4.7 cm and porosity 0.45 µm) grilled prior to the oven to maximally eliminate all organic traces.

Place a series of filters in de100ml flasks.

-Apply Filters with a clean glass rod.

-Add 2 ml of phosphoric acid.

-Cover with the crystallizer.

-Put in a sand bath at 100-110 ° C for 30 minutes.

-Add 10ml of chromic acid and cover again.

-Put in a sand bath for 30 to 60 minutes.

-Cool the flask.

-Add 50ml of distilled water and 2 drops of ferroin.

-Titrate with the Fe (II).

-Either V1 the volume in milliliters.

The determination of white: treat a series of three blank filters in the same way as above.

Averagepaid solution of Fe (II) volume V0 (threedeterminations).

Calibration of the solution so of Fe (II): check the title of the solution of Fe (II) using a solution of glucose, from the mother solution (solution of glucose) prepare a diluted solution (1 ml of stock solution adjusted to 100 ml) including 1 ml contains 300 µg of carbon. This solution does not keep for more than a day.

Take 5 ml of the secondary solution in a 100 ml erlenmeyer and oxidize them like filters, then Titrate is V'1 the corresponding Fe (II) volume (ml).

Titrate also 10 ml of mixture sulfochromique by the solution of ferrous sulfate.

Either V'0 (ml) the volume used.

- **Expression of results:**

Vf :the volume of water filtered.

V0 : volume of the titrant paid for white.

V1 :volume of the titrant paid for the sample.

F : calibration factor. The calibration factor F is obtained by:

$$F = \frac{1500}{(V'0 - V'1)}$$

The concentration of carbon organic particle is calculated as follows:

$[COP](\mu g.l^{-1}) = \frac{F(V0-V1)}{Vf}$

CHAPTER III

Beni-Haroun dam

CHAPTER III: DISTRIBUTION AND FLUXES OF WATER, PARTICULATE MATTER AND NUTRIENTS OVER THE KEBIR-RHUMEL CATCHMENT

1. Biogeochemical features at entrance and exit of Beni-Haroun dam and at the Kebir-Rhumel stream's mouth

The variability of the streams flow is directly related to the meteorological conditions and regulation by dams. The flow rate at Kebir-Rhumel (KR-M) stream's mouth largely varied between 3 and 160 $m^3 s^{-1}$ during the study period, according to the rainfall supply and Beni-Haroun dam regulation. Two major floods were recorded in February 2012 and February 2013 (Figure 14) as a result of heavy precipitation (197.5 mm in February 2012 and 180 mm in February 2013). Large incoming water discharge (150 $m^3 s^{-1}$) at the entrance of Beni-Haroun dam (KR-DO) was recorded during the flood of February 2012. At the exit of Beni-Haroun dam (KR-DE), the flow rate was reduced owing to the dam retention (Figure 14).

The mean level of TDS strongly fluctuated from one site to another of stream catchment. At KR-M, TDS levels varied between 193 and 2460 mg L^{-1} with an average of 591 mg L^{-1} during the study period (Figure 14; Table 3). At the entrance of Beni-Haroun dam the TDS values ranged from 323 and 1665 mg L^{-1} with an average of 674 mg L^{-1} during the study period. By the flood event period (February 2012) the TDS levels decreased to 384 mg L^{-1} (Figure 14). The Rhumel branch (R-DO) was more salinized, where values fluctuated between 349 and 1674 mg L^{-1} with an average of 1496 mg L^{-1}. At Beni-Haroun dam entrance the TSS amounts oscillated between 3 and 585 mg L^{-1}, with an average value of 91 mg L^{-1}. The TSS levels of the Rhumel stream branch (R- DO) largely fluctuated (3-488 mg L^{-1}), with an average of 72 mg L^{-1}. The exit of the Beni-Haroun dam had average annual levels of 54±24 mg L^{-1}, which is still low, compared to that of the Beni-Haroun dam entrance. Here the TSS retention rate reached 41%. Concentrations at the mouth largely fluctuated throughout seasons (1 and 472 mg L^{-1}) with an average annual of 73±30 mg L^{-1} (Table 3). By contrast to TDS, the TSS amounts increased (244 mg L^{-1}) during the flooding event of late February 2012.

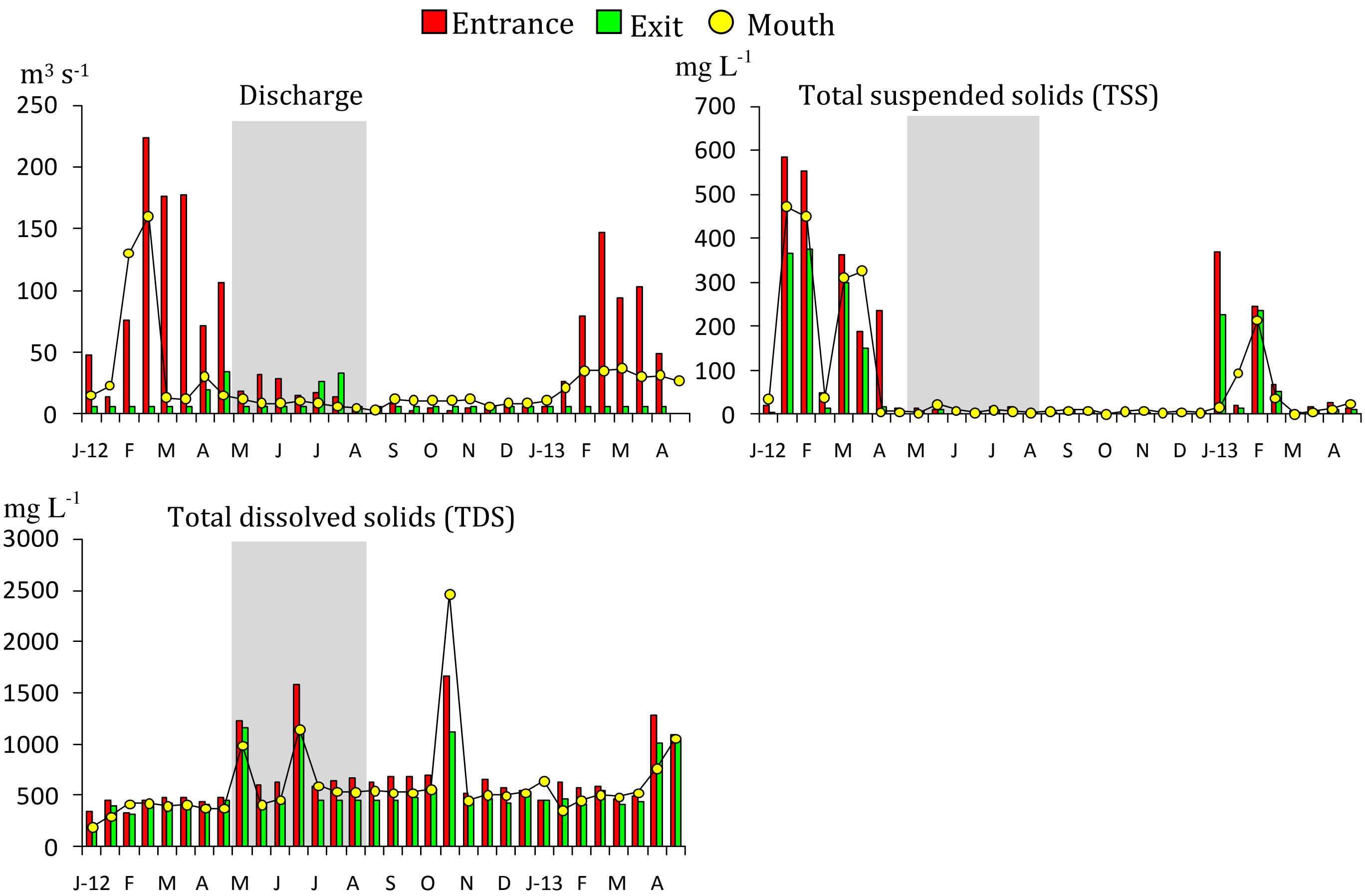

Figure 14: seasonal variations in hydrological parameters over the Kebir-Rhumel catchment during the study period, January 2012- April 2013.

At the entrance of Beni-Haroun dam, the total dissolved nitrogen (TDN) levels varied between 30-113 µmol L^{-1} with a mean of 61 µmol L^{-1} during the study period (Figure 15; Table 3). The dissolved organic form (DON) represented 30% (18 µmol L^{-1}) and the inorganic one (DIN = NO_3 + NO_2 + NH_4) formed 67%. Within the DIN nitrates (NO_3) and ammonium (NH_4) formed the major fraction with 29%, 33%, respectively; nitrite (NO_2) contributed only for 5% (Figure 15). Not only does the levels of NH_4 at the entrance were low compared to those of NO_3, but experienced large reduction rate retention rate (51%) within the dam compared to NO_3 (30%) as shown in Tables 4, and 5. This suggests that there would be some endogenous denitrification which would transform some fraction of NO_3 in NH_4. In contrast, the DON was released by the dam, and increased at the dam exit to 30 µmol L^{-1} during the study period (Table 3). This production may be related to the release of DON from the endogenous plankton growth and cycle.

Table 3: hydrological and biogeochemical parameters (mean ± standard error) at the entrance and exit of Beni-Hroun dam and at the Kebir-Rhumel stream's mouth, for the annual cycle January-December 2012. Mean values of particulate materials (BSi and POC) have been computed for the period March 2012-February 2013. Rr is the reduction rate of a given parameter by Beni-Hroun dam. Positive Rr indicated a release.

	Beni-Haroun dam						Kebir-Rhumel stream	
	Opening		Exit		Rr (%)	Rr* (%)	Mouth	
	2012	2013*	2012	2013*	2012	2013*	2012	2013*
Discharge	44±13	72±15.9	9±2	6±0.1	-79	-92	22.60±8	28.37±2.88
TSS	91±35	97.5±44.8	54±24	70.6±33.3	-41	-28	73±30	50.2±23.9
TDS	666 ±70	697±103.6	517±50	593.5±88.9	-22	-15	591±90	598.5±73.2
TDN	61±5.28	53.84±6.1	52.04±5.21	57.26±6.3	-15	+6	54.17±7.16	55.38±6.9
DIN	44±4.56	31.9±4.4	25.29±9.93	22.6±2.6	-43	-28	35.70±6.10	92.2±2.6
DON	17±1.65	21.91±2.75	28±3.04	34.68±4.15	+65	+59	18.47±1.85	26.19±5.95
NH_4	21±1.37	8.55±0.64	9.52±1.23	6.40±0.75	-55	-33	16.83±2.96	8.49±0.92
NO_3	20±3.84	21.18±4.60	14.35±3.18	14.87±2.65	-30	-29	17.01±4.42	18.95±2.76
NO_2	3.51±0.38	2.21±0.26	1.42±0.31	1.31±0.23	-59	-50	1.86±0.41	1.75±0.33
TDP	5.44±0.32	4.95±0.38	5.82±0.36	5.61±0.45	+7	+20	4.90±0.82	5.66±0.76
DIP	3.13±0.24	2.62±0.32	2.25±0.32	3.38±0.34	-28	+29	2.09±0.42	2±0.27
DOP	2.31 ±0.26	2.33±0.51	3.57±0.38	3.23±0.58	+54	-50	2.82±0.73	3.66±0.83
PO_4	2.45±0.23	2.11±0.32	1.86±0.21	2.07±0.32	-24	-2	1.67±0.41	1.51±0.29
$Si(OH)_4$	69.17±4.60	86.14±9.89	54±3.73	74.11±2.20	-22	-14	68.19 ±4.2	94.12±14
BSi	2.56±0.25	3.20±0.27	4.24±0.45	5.01±0.45	+66	+57	2.69±0.57	4.25±0.68
POC 1	1.55±0.15	2.10±0.23	2.65±0.26	3.19±0.28	+71	+52	2.65 ±2.21	2.24±0.11
POC 2	1.76±0.19	2.74±0.18	2.79±0.29	3.84±0.30	+59	+40	2.92±0.27	2.70±0.26
POC t	3.31±0.33	4.84±0.40	5.49±0.58	6.67±0.53	+66	+38	5.57±0.44	4.94±0.29
N :P	18	15	14	11			21	61
Si:N	1.5	3	2	3			1.9	1
Si:P	28	43	29	37			41	62

*: average of January, February March and April

At the Kebir-Rhumel mouth, the maximum level of TDN was found in the wet season (Figure 15). The DIN values varied between 10-129 µmol L^{-1} with a mean annual of 35.70±6.10 µmol L^{-1} and represented 67% the TDN amount. Within the TDN compounds, NO_3 formed 31% and NH_4 contributed to 30% as shown in table 3. The nitrogen dissolved organic form (DON) largely contributed to TDN with 33%, with maximum values encountered during springtime.

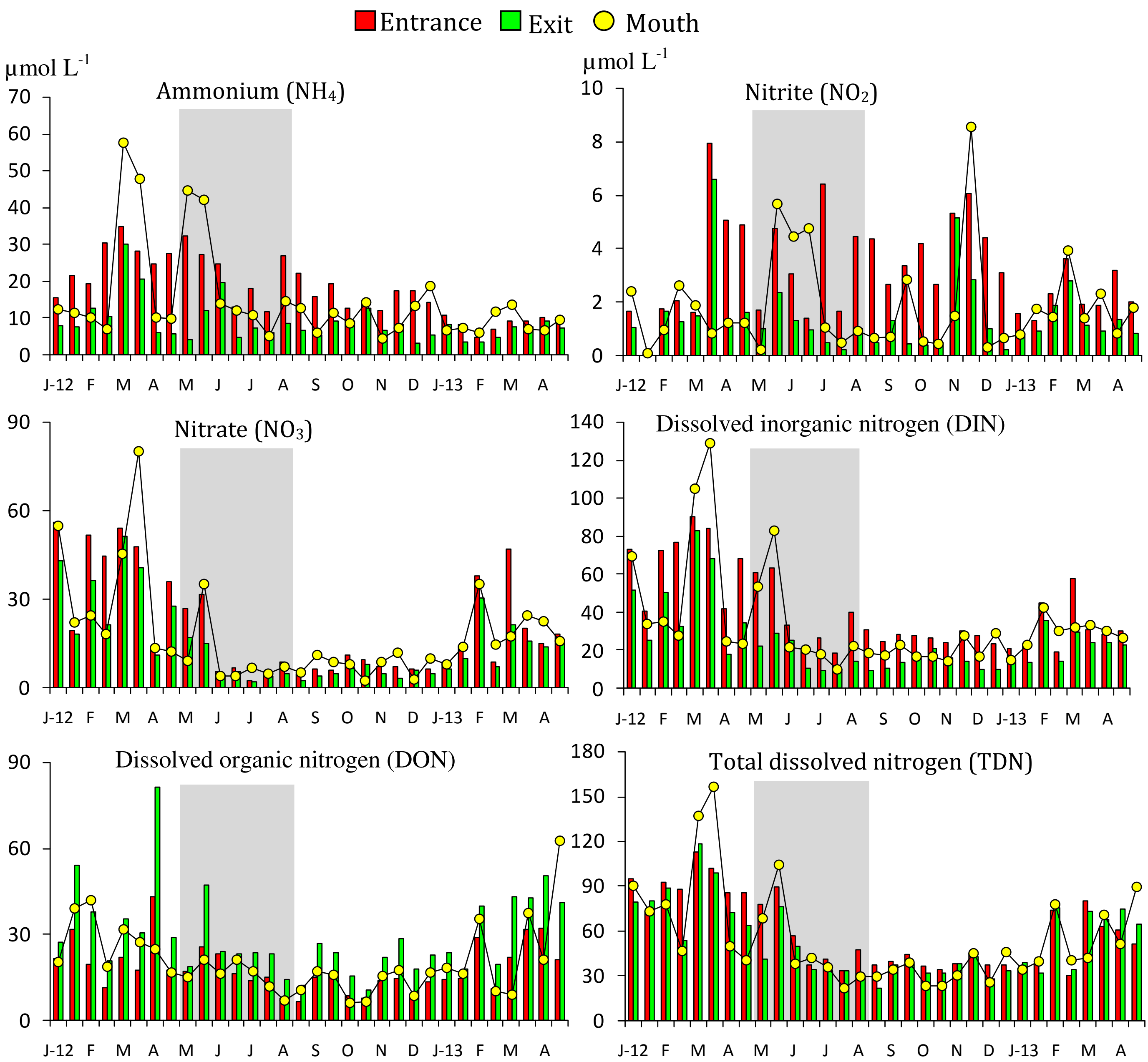

Figure 15: seasonal variations in the different forms of nitrogen over the Kebir-Rhumel catchment during the study period, January 2012- April 2013.

Concentrations of total dissolved phosphorus (TDP) at entrance of the dam varied between 2.02-9.09 µmol L^{-1} with an average annual of 5.44±0.32µmol L^{-1} (Table 3). At the entrance of the dam values of phosphates (PO_4) fluctuated between 0.72-4.78 µmol L^{-1} with a mean annual of 2.45±0.23µmol L^{-1}. Its fraction represented 45% the TDP. Because of its high removal within the dam, the PO_4 levels decreased at the dam exit by 24% and its mean value was lowed to 1.86±0.21µmol L^{-1}. This contrasts to the DOP form which was released by the dam at 54%.

Concentrations of silicates $Si(OH)_4$ at the entrance of Beni-Haroun dam fluctuated between 37-139 µmol L^{-1} with a mean of 69.17±4.60 µmol L^{-1}. However, the dam released low values at its exit (26-97 µmol L^{-1}) with an average annual of 54±3.73 µmol L^{-1} (Figure 16; Table 3). The dam had then reduced the incoming waters concentration by 22%.

During the study period levels of $Si(OH)_4$ fluctuated between 88-144 µmol L^{-1} with a mean of 73 µmol L^{-1}, showing no relation to the hydrological cycle and the stream flow. This is because of the dam effects. A large pick however exists after the high river flow during March 2013 and in lesser degree during the wet period of 2012. The waters crossing Kebir-Rhumel mouth were rich in $Si(OH)_4$ (75 µmol L^{-1}) and fluctuated between 25-194 µmol L^{-1}.

As for $Si(OH)_4$, the dissolved phosphorus compounds have no clear seasonal cycle (Figure 16), excepting the DOP which peaked during the high river flow of February 2012 and 2013. PO_4 levels varied between 0.11 to 9.3 µmol L^{-1} with an average annual of 1.67±0.41 µmol L^{-1} (Table 3). The TDP values fluctuated between 0.80 to 13.42 µmol L^{-1} with an annual average of 4.90±0.82 µmol L^{-1}. The DOP form was always the main component of the TDP forming 58% (2.82±0.73µmol L^{-1}), and the PO_4 fraction did not exceed 34%. At the Kebir-Rhumel mouth the molar ratios TDN:TDP was about 11, NO_3:PO_4 reached 10 and DIN:PO_4 was 22. Also, the Si: P was higher than the Redfield standard ratio (20) and reached 41 (Table 3).

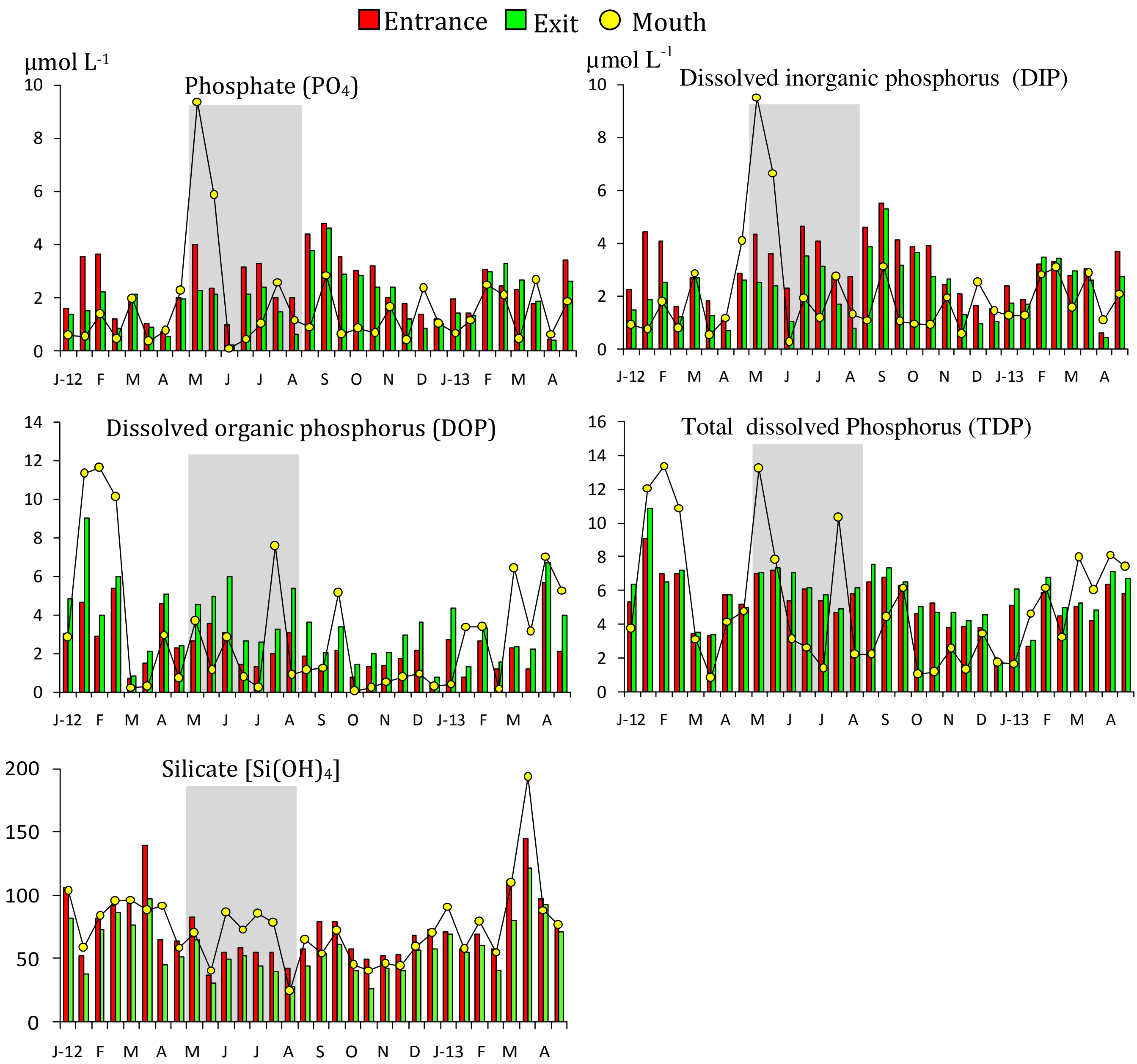

Figure 16: seasonal variations in the different forms of phosphorus and silicate over the Kebir-Rhumel catchment during the study period, January 2012- April 2013.

The dam received low levels of particulate silica (BSi) varying in range 1.1-6.93 µmol L^{-1} with a mean of 2.56±0.25 µmol L^{-1} (Figure 17; Table 3). By contrast, the BSi level has been increased by 66% at the dam exit (Tables 3; 4), owing to the endogenous diatom cycle. Though, the ratio BSi: $Si(OH)_4$ was very low both for the receiving (3.7%) and exiting (7.8%) waters. This implies that most of $Si(OH)_4$ was stored in dam, perhaps inside the local sediment.

The POC levels at the dam entrance largely varied, the POCt ranged from 0.97-6 mg L^{-1} with a mean of 3.31±0.33 mg L^{-1} (Figure 17; Table 3). The POC2 amount fluctuated between 0.57 and 3.54 with an annual mean of 1.76±0.19 mg L^{-1}, and POC1 varied between 0.40-2.94 mg L^{-1}. The two POC fractions were almost equally represented (POC1/POC2=0.88-0.94). As for the particulate silica, the POCt levels have been increased by 55% behind the dam as a result of the biological production.

Table 4: retention rates (%) at Beni-Haroun dam. Negative values (-) denote reduction rate and positive ones (+) denote release.

	NH_4	NO_3	NO_2	DIN	DON	TDN	PO_4	DIP	DOP	TDP	$Si(OH)_4$	BSi	POC 1	POC 2	POCt	TSS	TDS	Q
Ja-12	-49	-38	-24	-29	+26	-17	-14	-45	+44	+19	-23					-99	-56	-88
	-65	-75	-7	-38	+72	+10	-77	-73	+98	+20	-28					-37	-10	-59
Feb	-35	-5	-29	-30	+95	-4	-39	-37	+38	-7	-12					-32	-2	-92
	-66	-39	-53	-57	+85	-39	-22	-21	+7	+3	-5					-75	-2	-97
Mar	-13	-8	-5	-8	+60	+5	-11	-16	+27	+3	-22	+83	+87	+89	+55	-17	-10	-97
	-27	-17	-15	-35	+76	-19	-51	-52	+58	+2	-30	+74	+100	+74	+89	-21	-9	-97
Apr	-76	-78	-11	-57	+25	-16	-27	-42	+7	+1	-31	+81	+90	+92	+91	-93	-6	-73
	-80	-67	-23	-49	+66	-26	-4	-12	+1	-4	-20	+41	+78	+47	+61	-85	-6	-68
May	-88	-43	-36	-64	+12	-47	-18	-18	+29	+1	-22	+78	+104	+70	+40	-42	-6	-69
	-55	-51	-53	-54	+83	-14	-35	-48	+82	+2	-17	+62	+78	+60	+77	-11	-30	-82
Jun	-21	-57	-20	-24	+4	-12	-77	-49	+70	+31	-49	+86	+63	+51	+90	-76	-31	-80
	-64	-32	-16	-47	+41	-8	-28	-21	+61	+2	-10	+73	+26	+99	+99	-47	-30	-62
July	-60	-93	-24	-65	+70	-19	-30	-26	+93	+6	-20	+64	+80	+76	+98	-57	-23	+57
	-49	-87	-29	-47	+57	-1	-22	-34	+70	+5	-41	+95	+47	+5	+23	-91	-30	-133
Aug	-68	-78	-48	-65	+86	-41	-68	-73	+40	+6	-34	+27	+51	+82	+53	-26	-33	+70
	-70	-90	-50	-69	+96	-42	-30	-31	+54	+16	-22	+28	+85	+95	+90	-28	-29	+79
Sep	-66	-52	-37	-57	+76	-7	-28	-24	+79	+9	-32	+75	+78	+36	+56	-16	-34	-24
	-53	-87	-20	-50	+47	-15	-56	-56	+96	+3	-23	+97	+69	+91	+79	-78	-31	+131
Oct	-28	-91	-39	-42	+87	-12	-24	-18	+47	+9	-29	+82	+93	+84	+17	-43	-19	+27
	-13	-83	-17	-21	+41	-7	-21	-28	+26	-10	-47	+23	+50	+37	+72	-45	-33	+123
Nov	-44	-3	-33	-32	+60	+1	-17	-21	+67	+24	-18	+20	+87	+49	+77	-30	-14	+26
	-53	-53	-54	-53	+94	-5	-65	-66	+97	+11	-23	+70	+57	+60	+48	-87	-28	+12
Dec	-82	-77	-5	-64	+96	-25	-64	-63	+73	+21	-18	+41	+57	+12	+29	-70	-26	-17
	-63	-93	-26	-57	+71	-11	-61	-44	+69	+7	-21	+82	+53	+69	+77	-35	-3	+9
Ja-13	-23	-48	-29	-27	+65	+10	-28	-28	+88	+48	-2	+39	+84	+13	+20	-39	-1	+8
	-58	-32	-32	-41	+22	-17	-23	-32	+80	+30	-5	+28	+92	+51	+60	-42	-25	-77
Feb	-29	-20	-19	-20	+38	+2	-28	-33	+94	+40	-13	+78	+70	+69	+80	-4	-28	-93
	-33	-23	-18	-24	+76	+12	-5	-31	+66	+10	-29	+50	+93	+34	+8	-24	-9	-96
Mar	-16	-42	-55	-48	+98	-8	-50	-47	+88	+5	-28	+50	+14	+10	+28	-62	-12	-94
	-16	-52	-21	-21	+35	+7	-21	-31	+85	+15	-16	+75	+45	+46	+27	-52	-13	-94
Apr	-11	-57	-8	-15	+57	+23	-10	-45	+16	+12	-5	+68	+2	+54	+68	-60	-22	-88
	-25	-59	-18	-23	+96	+26	-24	-27	+39	+16	-8	+67	+88	+47	+28	-25	-5	

At the Kebir-Rhumel mouth, POCt concentrations varied from 1.46-9.26 mg L^{-1} with an annual average of 5.57±0.44 mg L^{-1} (Figure 17). POC1 represented a fraction of 48% and POC2 represented 52%. These values still largely comparable to those recorded behind Beni-Haroun dam.

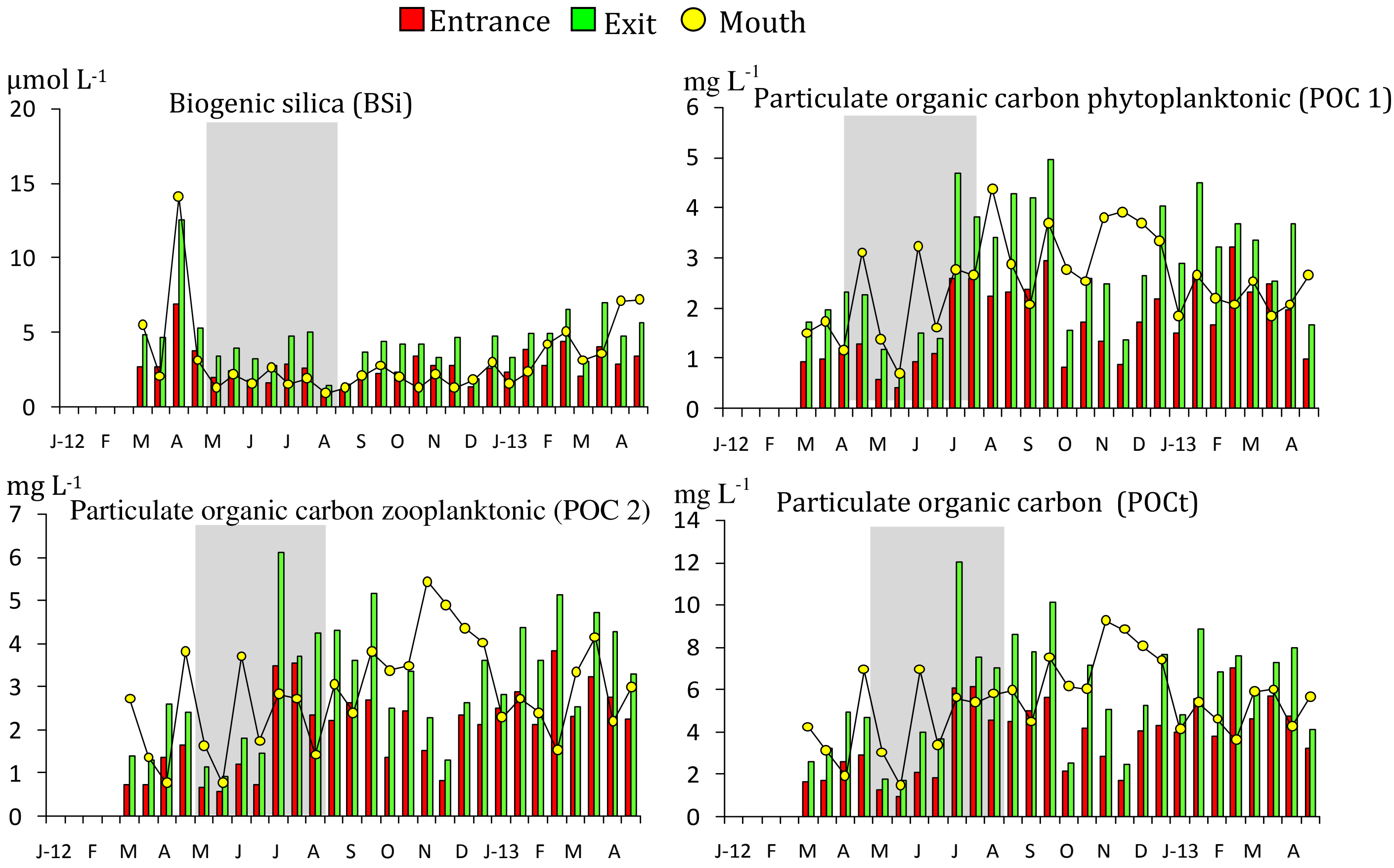

Figure 17: seasonal variations in biogenic silica and particulate organic Carbone over the Kebir-Rhumel catchment during the study period, January 2012- April 2013.

2. Fluxes of water, TDS, TSS, dissolved nutrients and particulate matter over the Kebir-Rhumel catchment.

As 2012 was exceptionally wetted, the Beni-Haroun dam has received strong water volume reaching an amount of 1382 10^6 m^3, ever recorded. From this volume, 111 10^6 m^3 served for drinking water, 228 10^6 m^3 for irrigation and 295 10^6 m^3 delivered behind the dam, and 748 10^6 m^3 has been stored in the dam (Table 5). About third the received water volume was brought during the flood of late February. The freshwater discharge into the sea from KR-M was 705.10^6 m^3 yr^{-1} (Table 5) from which 53% was due to the flood inputs.

The strong delivered water into Beni-Haroun dam brought annually 238000 tons of suspended sediment, from which 95% is lost to the dam (Table 5). The flooding of

February alone contributed to 65000 tons of sediment, which represents 27% the annual load. During the same flooding, the Beni-Haroun dam exported 78000 tons to the lower catchment. The erosion rate was elevated (14000 kg km^{-2} yr^{-1}) during this rainy year in the sub-catchment (Table 5). This difference is mainly due to the large amount of water discharge from the entrance of Beni-Haroun dam, and the exceptionally elevated rainfall height over Beni-Haroun sub-catchment. Some other geological characters (land cover, basin slope and soil nature) may be responsible for this variation.

Table 5: fluxes of water, sediment (TSS), salts (TDS), dissolved nutrients and particulate matter (t yr^{-1}) from and into Beni-Haroun dam and at the respective stream's mouth during 2012. The contribution of the flood event of February 2012 is also indicated Q: water volume. DW: volume of drinking water; IW: volume of irrigated water. Negative values (-) denote retention rate and positive ones (+) denote release.

	Beni-Haroun dam						Kebir- Rhumel stream		
	Opening (t yr^{-1})	Flood (t yr^{-1})	Exit (t yr^{-1})	Flood (t yr^{-1})	R/P (%)	Flood R/P (%)	Mouth (t yr^{-1})	Flood (t yr^{-1})	Yield (kg km^{-2} yr^{-1})
Q (10^6 m^3)	1382	390	295	16	-79	-96	705.3	377	
DW (10^6 m^3)			111						
IW (10^6 m^3)			228						
NH_4	527	140	76	2.2	-86	-98	126	41	16
NO_2	71	10	11	0.5	-85	-95	18	9	2
NO_3	768	235	97	6	-87	-97	199	103	25
DIN	1366	385	184	8	-86	-97	343	153	42
DON	374	68	240	6	-36	-91	247	142	30
TDN	1740	452	425	14	-76	-96	590	295	73
PO_4	78	20	17	1	-78	-95	27	9	4
TDP	228	79	52	3	-77	-96	191	131	24
DIP	106	25	21	1	-80	-96	36	13	4.5
DOP	122	54	31	1	-74	-98	154	118	19
$Si(OH)_4$	1288	908	872	11	-32	-98	1609	885	198
BSi	98		65		-34		37		5
POC 1	1240		1140		-8		817		101
POC 2	1273		1256		-1		923		114
POCt	3164		2396		-24		1740		215
TSS (10^3)	238	65	11	5	-95	-92	112	78	14000
TDS (10^3)	687	155	146	6	-79	-96	351	1	43163
POC t/TSS	1		22				1.5		
N:P	18		11				13		
Si:N	1		5				5		
Si:P	16.5		51				59		

As shown in table 5, the dam received 687000 t yr^{-1} of TDS. Beni-Haroun dam retained 79% of the received mass. The stream's mouth delivered to adjacent coast 351000 t yr^{-1} of TDS (Table 5). The soils of the Kebir-Rhumel were then subject to large salts loss, reaching 43000 kg km^{-2} yr^{-1}. The Kebir-Rhumel mouth delivered annually into the sea 351000 tons of TDS. It seems that during this heavily rainfall year, the soils of KR catchment have been subject to large fertility loss regarding the salts, sediments, nutrients and POC. In addition, our results clearly shows that Beni-Haroun dam acts as like-filters by trapping large masses of dissolved inorganic nutrients, sediment and salts (Table 5). It can be seen that DIN experienced strong removal (86%) at Beni-Haroun dam. Among the DIN forms, N-NH_4 was widely preferentially retained at rates 86% in the Beni-Haroun dam (Table 5). Similarly, 78% of the received P-PO_4 masses have been lost to the dam. However for Si-$Si(OH)_4$ and BSi, only third the incoming amount was trapped within the dam. Consequently, great masses (1600 t yr^{-1}) reached then the KR-M and transferred to the sea. Here the flood of late February contributed significantly, bringing into the sea around 900 tons of Si-$Si(OH)_4$ (Table 5). Among the nutrients, the most important loads into and from the dam and into the sea was in the form of organic particulate carbon (POC), as can be seen in table 5. The dam has been invaded by large masses of POC (3164 t yr^{-1}), but has only 24% of that load. An important load has been also transferred into the sea from the KR-M. On the one hand, this is equivalent to a specific load (yield) of 215 kg km^{-2} yr^{-1} but represented, on the other hand, only 1.5% the sediment discharge.

CHAPTER IV

CHAPTER IV: WATER DISCHARGE, SEDIMENT, PARTICULATE MATTER AND NUTRIENT CONCENTRATIONS AND FLUXES OVER THE KEBIR WEST CATCHMENT

1. Biogeochemical features at entrance and exit of Zit Amba dam and at the Kebir West stream's mouth

Kebir West catchment has received large precipitation between September 2012 and April 2013 (488 mm), which has directly increased the surface water flow across the catchment. The water flow rate at Kebir West stream's mouth (KW-M) increased to over 80 $m^3\ s^{-1}$ during the flood of February 2012 (Figure 18). The low river flow extended from May-September (7.3 $m^3\ s^{-1}$). However, the mean river discharge (17.3 $m^3\ s^{-1}$) at KW-M was not much different regarding the discharge delivered into the dam (Table 6). The water flow entering Zit Amba dam (KW-DO) had varied between 0.5-88 $m^3\ s^{-1}$ with an average of 14.1 $m^3\ s^{-1}$ during the study period. The exit of the Zit Amba dam (KW-ED) released in average about half the received discharge (7.6 $m^3\ s^{-1}$) as can be seen in figure 18 and Table 6.

The water concentrations of TDS at KW-M varied between 260-5752 mg L^{-1}, with an average of 1853 mg L^{-1} (Figure 18; Table 6). The KW-M station is affected by marine tidal intrusion, when river flow decreased during the dry period. By such condition, the TDS increased to 2283 mg L^{-1}. The lowest value (274 mg L^{-1}) was recorded during the stream flood of February 2012 (Figure 18) when the mouth area is connected to the surrounding swamp of Sanhaja. The TDS concentration at the entrance of Zit Amba dam ranged from 182-1298 mg L^{-1}, with an average amount of 540 mg L^{-1} during the study period. The dam reduces this amount by 30%; and the he TDS concentration at the dam' exit decreased to 400 mg L^{-1}, as shown in Figure 18 and Table 6.

TSS levels at the entrance of Zit Amba dam were the lowest among the studied sites, and varied between 4.9-66.3 mg L^{-1}, with an average annual of 16 mg L^{-1} (Figure 18; Table 6). Moreover, the average concentration did not exceed 11.3 mg L^{-1} at the exit of Zit Amba dam. This dam has decreased by 40% the incoming amount (Tables 6; 7). At KW-M the average concentration was 28 mg L^{-1} during the study period, but increased to 37 mg L^{-1} during the wet period.

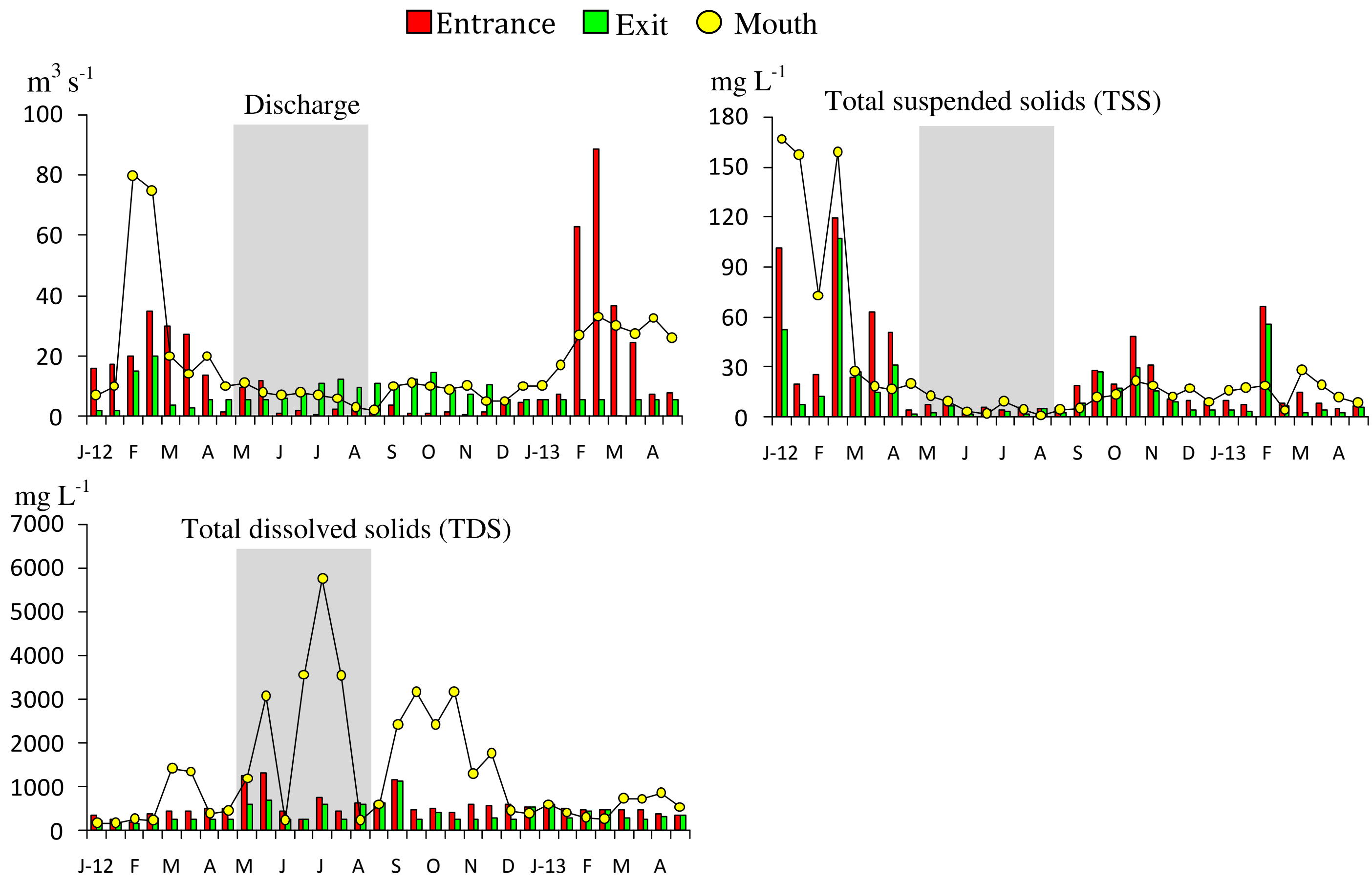

Figure 18: seasonal variations in hydrological parameters over the Kebir West catchment during the study period, January 2012- April 2013.

During the study period, levels of the total dissolved nitrogen (TDN) at the entrance of Zit Amba dam varied between 18-106 µmol L^{-1} (Figure 19) with an annual average of 50.52±4.90 µmol L^{-1} (Table 6). Most of TDN amount was in the form of NO_3 (39%) and NH_4 (27%); the DON contributed only by 26%. Throughout the seasons, the DIN levels varied between 13-86 µmol L^{-1} with an average of 37 µmol L^{-1} during the study period (Figure 19; Table 6). As shown in table 7 the DIN amount decreased by 32% at the dam exit but the DON amount increased by 56%. In particular, NH_4 was retained at high rate (36%) within the dam and in a lesser degree NO_3 (26%). The delivered waters at the exit of the dam were then lowered in term of DIN but enriched with DON. At the entrance of Zit Amba dam the DON levels ranged from 5-27 µmol L^{-1} (Figure 19) with an annual average of 13.53±1.50 µmol L^{-1} and a maximum during the wet period (Figure 19).

Table 6: hydrological and biogeochemical parameters (mean ± standard error) at the entrance and exit of Zit Amba dam and at the Kebir West stream's mouth, for the annual cycle January-December 2012. Mean values of particulate materials (BSi and POC) have been computed for the period March 2012-February 2013. Rr is the reduction rate of a given parameter by Zit Amba dam. Positive Rr indicated a release.

	Zit Amba dam						Kebir West stream	
	Opening		Exit		Rr (%)	Rr* (%)	Mouth	
	2012	2013*	2012	2013*	2012	2013*	2012	2013*
Discharge	6.1±2.12	30.08±11	8.21±0.9	5.10±0.69	-35	-83	9.31±4.03	25.42±2.80
TSS	18.4±6.23	16.05 ±7.2	11.1±4.70	11.13±6.40	-40	-31	12 ±10.4	15.4 ±2.58
TDS	616 ±59.3	461.9±26.7	412±46.7	369±42.3	-33	-20	1853±305	566 ±75
TDN	50.52±4.90	49.59±8.01	45.02±4.90	49±8.37	-12	-2	50.51±4.90	49.14±9.24
DIN	37±4.51	36.24±6.10	24.92±3.16	25.74±3.92	-32	-28	35.61±3.72	33.82±6.47
DON	13.53±1.50	13.35±2.50	20.10±1.99	23.83±5.91	+49	+85	14.89±1.20	15.31±3.43
NH_4	13.68±1.43	13.32±2.17	8.59±1.05	8.88±0.67	-37	-32	13.12±1.11	13.31±2.35
NO_3	19.71±4.14	20.39±4.19	14.53±2.98	15.46±3.44	-26	-25	19.77±3.90	19.07±4.64
NO_2	3.61±0.43	2.35±0.42	1.80±0.25	1.41±0.20	-50	-40	2.73±0.35	1.44±0.30
TDP	5.04±0.37	5.28±0.33	5.29±0.44	5.94±0.37	+5	+20	4.70±0.66	5.62±0.69
DIP	2.92±0.25	3.62±0.32	2±0.27	2.93±0.31	-32	-25	2.26±0.27	3.91 ±0.70
DOP	2.12±0.33	1.66±0.24	3.29±0.43	3.01±0.51	+55	+8	2.44±0.68	1.71±0.45
PO_4	2.13±0.25	3.04±0.35	1.36±0.22	2.10±0.40	-36	-33	1.58±0.22	2.98±0.51
$Si(OH)_4$	80.21±5.09	91.7±15.44	57±2.79	67.30±9.51	-29	-27	74.48 ±3.52	90.23±14.7
BSi	2.41±0.54	3.38±0.34	4.02±0.78	6.35±0.36	+67	+88	2.3 ±0.31	5.21±0.88
POC 1	1.6±0.19	1.42±0.15	2.53±0.28	2.63±0.26	+58	+85	1.89±0.20	2.68 ±0.41
POC 2	1.84±0.22	1.88±0.25	2.7±0.31	3.30±0.42	+47	+76	2.18±0.23	3.31±0.40
POC t	3.30±0.40	3.40±0.40	5.5 ±0.68	5.23±0.58	+67	+54	5.99±0.79	4.0±0.43
N: P	17	12	18	12			22	11
Si:N	2	3	2.2	2.63			2	2.66
Si:P	38	30	42	32			47	30

*: average of January, February March and April.

As shown in figure 19 values of NO_3 of waters entering Zit Amba dam varied from 1-73 µmol L^{-1} with an average of 20 µmol L^{-1} during the study period (Table 6). This amount decreased at the exit by 25% to reach 15 µmol L^{-1}. The highest levels of NO_3 were recorded during the wet period. Zit Amba dam received high levels of NH_4 (14 µmol L^{-1}), which represented 28% of TDN. During the dry period, concentrations of NH_4 increased to 15 µmol L^{-1} at the entrance and 11 µmol L^{-1} at exit. At the entrance of the dam the seasonal evolution of NO_2 varied between 0.4-9 µmol L^{-1} (Figure 19) with an annual average of 3.3 µmol L^{-1} during the study period (Table 6) only representing 7% of TDN. Concentrations of NO_2 at the exit decreased by half the incoming stock (Tables 6; 7). At the KW-M the dissolved nitrogen levels followed clear seasonal variations reaching high values during the wet period and lower values from late spring until early autumn. The TDN levels of of Kebir West stream's mouth had an average concentration of 50 µmol L^{-1} during the study period, where DIN dominant was the dominant form (35 µmol L-1, Table 6), representing 70% of the TDN (Figure 19). During the wet period the

TDN average concentration was 53 µmol L^{-1}, with DON formed 30%. By dry period the average concentration decreased to 42 µmol L^{-1} from which the DIN represented 74%. Within DIN forms, NO_3 was more abundant in all seasons, forming about third the dissolved nitrogenous stock (20 µmol L^{-1} in average) (Figure 19).

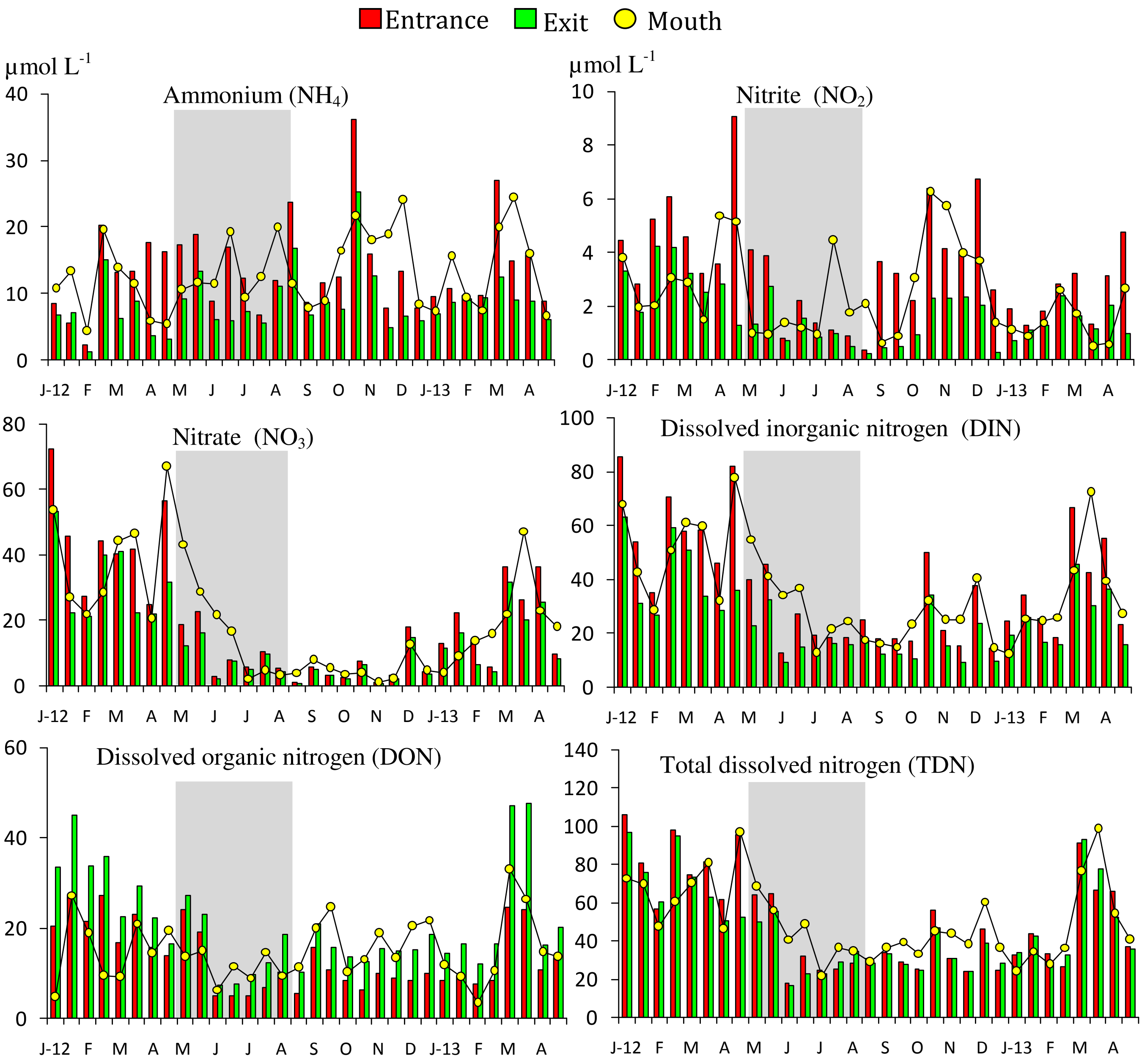

Figure 19: seasonal variations in the different forms of nitrogen over the Kebir West catchment during the study period, January 2012- April 2013.

The TDP average concentration was 5.10 µmol L^{-1} during the study period at the entrance of Zit Amba dam (Figure 20; Table 6). The organic fraction or DOP represented 40% with an average concentration of 2.01 µmol L^{-1}. At the entrance of the Zit Amba dam concentration of PO_4 showed a clear spatial and temporal distribution, varying between 1-6 µmol L^{-1} (Figure 20), with an average of 2.36 µmol L^{-1} during study period (Table 6). In contrast, at the exit the levels deceased by 34% to reach 1.55 µmol L^{-1} (Tables 6; 7), while the DOP is released and increased by 60% (Tables 6; 7).

At the entrance of Zit Amba dam, the average concentration of silicates $Si(OH)_4$ during the study period was relatively elevated (83 µmol L^{-1}) but haven't experienced large reduction (29%; Tables 6; 7). It was lowered to 60 µmol L^{-1} at exit of the dam (Figure 20). Paradoxically, at the entrance of the dam concentration of $Si(OH)_4$ during the wet period reached 87 µmol L^{-1} in average and were increased in the dry period (94 µmol L^{-1}).

Kebir West stream's mouth had relatively low levels of PO_4, with an average annual average of 1.58±0.22µmol L^{-1}. The average concentration in TDP was 4.70±0.66µmol L^{-1} in which the organic form represented 52% with an average annual of 2.44±0.68µmol L^{-1} (Figure 20; Table 6). The delivered waters into the neighboring coast were heavily loaded with TDP over all the study period. However, in the wet period the levels slightly increased to reach 5.3 µmol L^{-1}. There are some changes in the dry period where the average concentration decreased to 4.5 µmol L^{-1}, and the DOP fraction only represented 34%.

The average concentration in $Si(OH)_4$ was 78 µmol L^{-1} (Figure 20), and high levels were found in the dry period, reaching 68 µmol L^{-1}. The delivered waters from the KW-M were highly disturbed as N:P molar ratio (22) deviated from the Redfield standard ratio. In contrast, Si:N was more balanced and reached 2.

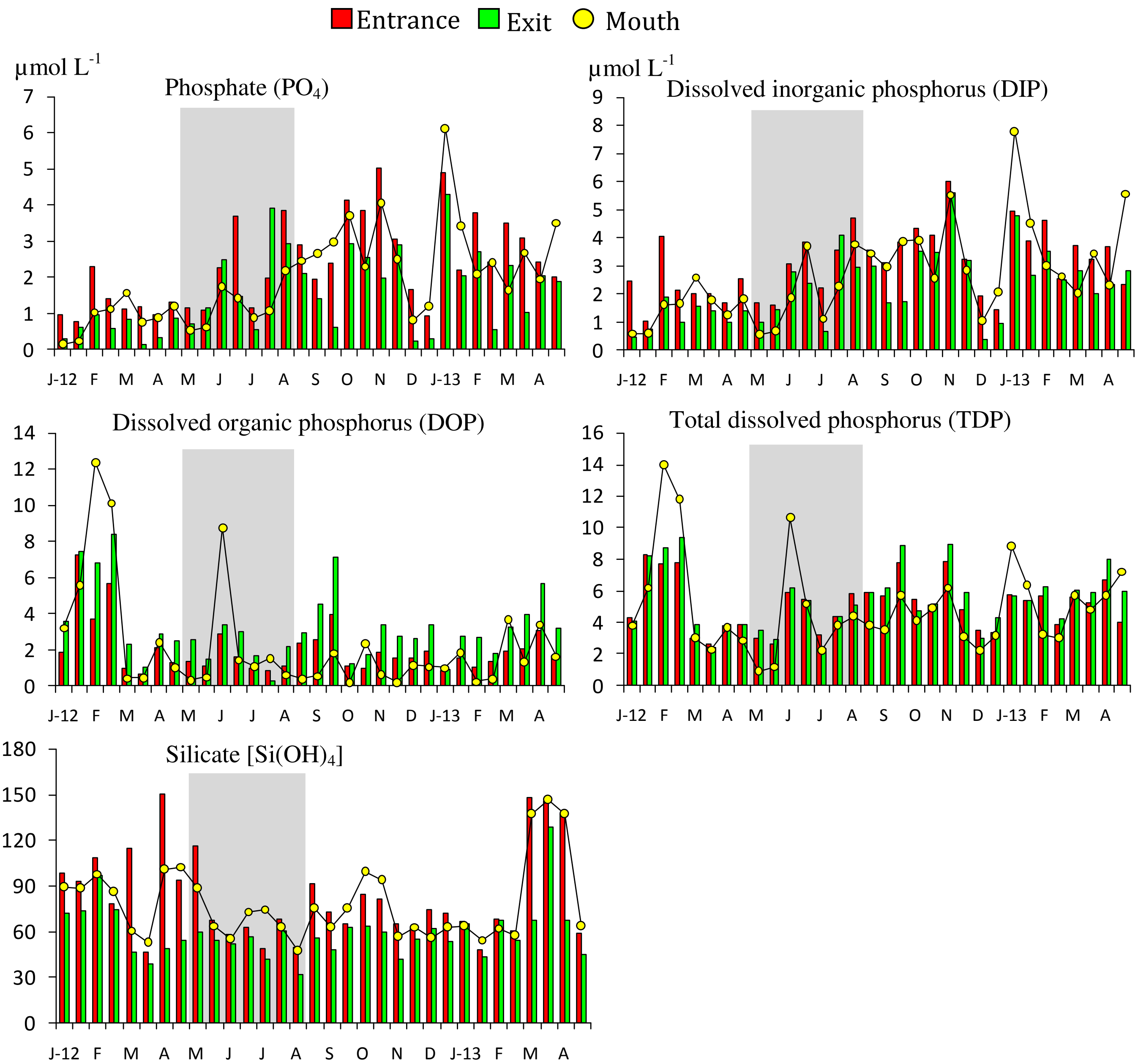

Figure 20: seasonal variations in the different forms of phosphorus and silicate over the Kebir West catchment during the study period, January 2012- April 2013.

Table 7: reduction rates (%) of the various hydrological and biogeochemical parameters at Zit Amba dam. Negative values (-) denote reduction and positive ones (+) denote release.

	NH_4	NO_3	NO_2	DIN	DON	TDN	PO_4	DIP	DOP	TDP	$Si(OH)_4$	BSi	POC1	POC2	POC1t	TSS	TDS
Ja-12	-22	-27	-26	-26	24	-9	-70	-81	+97	-5	-27					-48	-37
	+28	-51	-38	-42	67	-6	-19	-29	+3	-1	-21					-62	-34
Feb	-48	-22	-20	-24	58	+7	-58	-53	+85	+13	-11					-52	-11
	-26	-10	-31	-16	31	-3	-59	-55	+48	+20	-5					-10	-25
Mar	-52	+2	-30	-13	33	-2	-26	-23	+137	+28	-60	+125	+33	+74	+6	+16	-41
	-34	-47	-22	-42	27	-23	-88	-30	+61	-8	-16	+45	+6	+55	+86	-76	-42
Apr	-79	-11	-20	-38	+41	-18	-67	-41	+34	+1	-68	+93	+17	+13	+14	-38	-50
	-81	-44	-86	-56	+18	-45	-34	-46	+95	+1	-42	+15	+84	+33	+67	-44	-47
May	-46	-35	-68	-43	+13	-22	-39	-42	+91	+17	-49	+96	+102	+103	+55	-62	-53
	-29	-28	-29	-29	+20	-14	+6	-9	+37	+9	-19	+66	+66	+60	+89	-29	-46
Jun	-31	-29	-9	-29	+46	-8	+10	-9	+19	+5	-11	+44	+100	+72	+58	-62	-40
	-66	-6	-29	-45	+57	-30	-60	-38	+87	-1	-10	+86	+33	+13	+21	-26	-4
July	-40	-13	-38	-32	+94	-6	-52	-71	+70	-28	-13	+95	+31	+24	+28	-15	-19
	-20	-6	-11	-11	+85	+15	+99	+15	-66	+0	-11	+87	+87	+62	+73	-67	-40
Aug	-7	-23	-42	-13	+82	+21	-24	-38	+95	-12	-35	+92	+63	+50	+56	-5	-1
	-29	-32	-40	-29	+87	-8	-27	-16	+25	+0	-39	+77	+77	+94	+86	-48	0
Sep	-22	-12	-88	-33	+34	-2	-28	-46	+78	+9	-34	+59	+69	+86	+77	-55	-1
	-25	-9	-84	-33	+47	-3	-74	-55	+81	+14	-3	+61	+59	+23	+38	-3	-48
Oct	-38	-10	-58	-37	+63	-4	-29	-19	+11	+13	-25	+31	+100	+60	+83	-13	-23
	-30	-12	-64	-32	+99	-17	-34	-15	+73	+2	-26	+101	+94	+54	+69	-39	-38
Nov	-21	-55	-45	-27	+58	0	-61	-7	+80	+14	-35	+72	+72	+88	+71	-50	-55
	-38	-42	-43	-40	+66	-1	-6	-1	+76	+24	-11	+66	+79	+44	+60	-13	-52
Dec	-50	-17	-70	-38	+82	-16	-86	-81	+68	-15	-16	+90	+87	+76	+90	-58	-57
	-23	-16	-89	-33	+87	+16	-68	-35	+75	+28	-26	+71	+13	+4	+8	-45	-1
Ja-13	-28	-10	-64	-21	+71	+3	-12	-3	+6	-1	-2	+81	+74	+91	+57	-53	-1
	-19	-28	-14	-24	+77	-3	-8	-22	+83	+0	-10	+38	+75	+100	+88	-49	-44
Feb	-5	-55	-30	-34	+55	-13	-29	-24	+165	+10	-1	+92	+82	+58	+69	-16	-6
	-4	-26	-15	-12	+98	+22	-78	-2	+32	+9	-11	+97	+109	+60	+35	-18	-1
Mar	-54	-13	-49	-31	+91	+2	-33	-24	+72	+8	-55	+80	+92	+49	+65	-80	-40
	-40	-24	-15	-29	+98	+17	-67	-38	+94	+13	-12	+21	+75	+84	+80	-47	-43
Apr	-44	-30	-35	-34	+52	-20	-16	-36	+88	+20	-51	+53	+69	+73	+91	-35	-23
	-30	-13	-79	-33	+50	-3	-7	+22	+90	+25	-24	+82	+113	+112	+70	-4	-2

The entrance of Zit Amba dam showed low levels of POCt ranging from 0.2-7.2 mg L^{-1} with a mean of 3.4 mg L^{-1} during the study period. This amount formed 14% of the incoming TSS and may result in the fertility loss of the head catchment lands. The two fractions POC1 and POC2 have comparable levels (Figure 21; Table 6). POC1 levels varied between 0.12 to 3.25 mg L^{-1} with a mean of 1.5 mg L^{-1} during the study period and POC2 varied had an average of 1.8 mg L^{-1}. During the wet period the levels of POC2 increased to 2 mg L^{-1} (59% of the POCt).

At the entrance of the dam levels of BSi varied between 0.83 and 5.7 mg L^{-1} with a average annual of 2.41±0.54 mg L^{-1} (Figure 21; Table 6). The exit of the dam released large amount of this particulate material as for POC. The delivered waters have 66% more BSi compared to the incoming waters (Table 6; 7) owing the development of siliceous organisms (diatoms and various phytoliths).

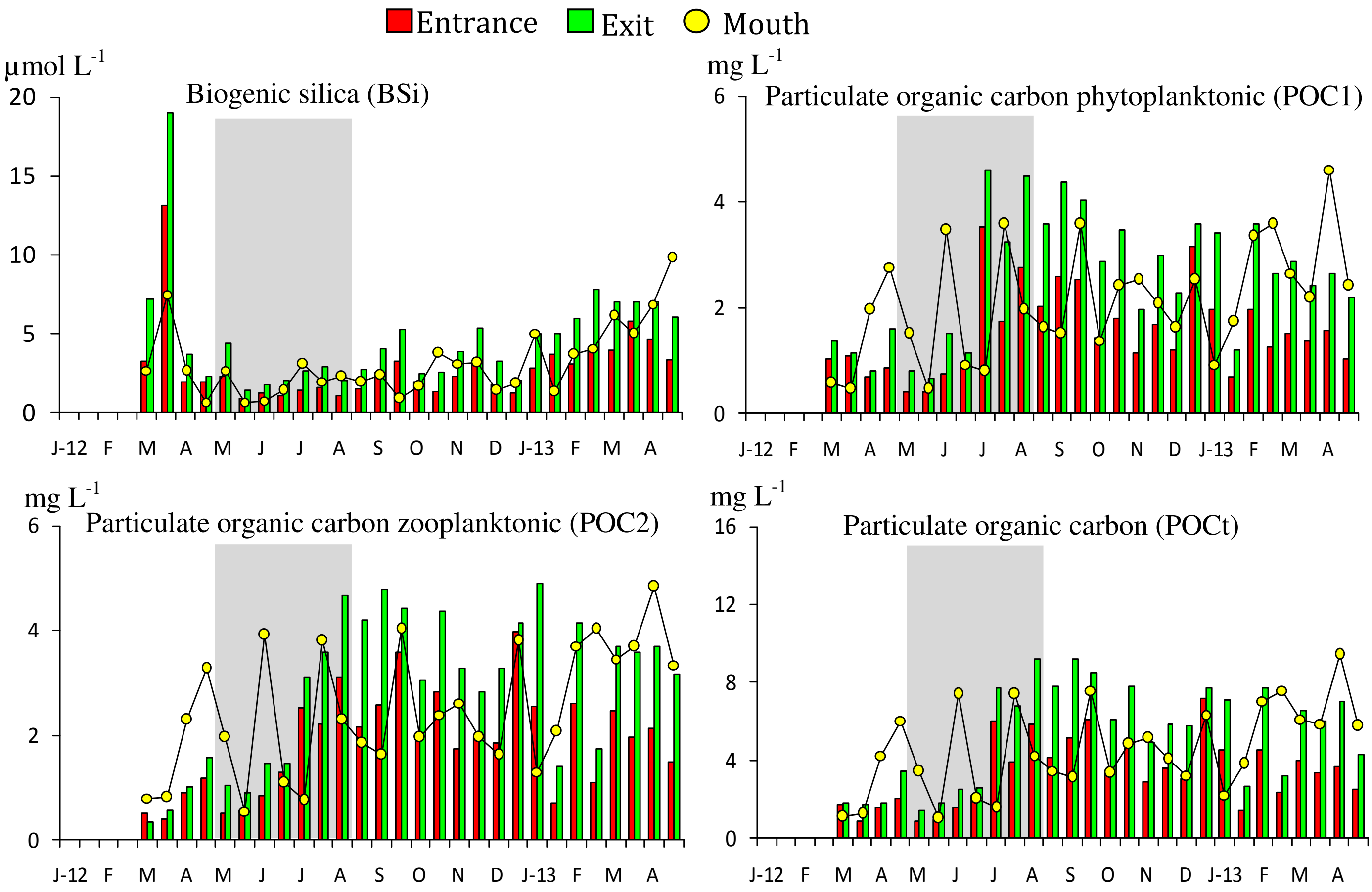

Figure 21: seasonal variations in biogenic silica and particulate organic matter over the Kebir West catchment during the study period, January 2012- April 2013.

As shown in figure 21, POCt levels averaged 4.6 mg L^{-1} during the study period at KW-M where the levels fluctuated between 1.01 and 9.46 mg L^{-1}. The POC1 represented 46% of total particulate organic carbon. The POC1 levels fluctuated during the study period between 0.46 and 4.62 mg L^{-1} with an average of 2 mg L^{-1} (Table 8). The POC2 still represented a comparable fraction and level (54% and 2 mg L^{-1}) within POCt. The BSi values fluctuated during the study period between 0.61 and 9.79 µmol L^{-1} with an average of 2.9 ± 0.4 µmol L^{-1} (Table 8). The maximum levels were found during spring, coinciding with the phytoplankton growth cycle as can be seen in figure 21.

2. Fluxes of water, TDS, TSS, dissolved nutrients and particulate matter across the Kebir-West catchment

Kebir West stream discharged into the sea 466.10^6 m^3 yr^{-1} of freshwater (Table 8) during 2012. As 2012 was highly wetted over the catchment, the dam has been completely filled, and consequently only 3% of the incoming water was retained in. Its residence time was only in the order of 4 months.

Zit Amba dam had received 14000 t yr^{-1} of TSS, from which 6000 t yr^{-1} was brought during the flooding event of February 2012. The dam has however removed 57% of the introduced mass (Table 8). However, as shown in table 8, the Kebir West stream's mouth transferred into the sea great amount of sediment (30500 t yr^{-1} of TSS).

Also, the dam received 134500 t yr^{-1} of TDS, from which 23% was retrained (Table 8). The stream's mouth delivered to adjacent coast 496000 t yr^{-1} of TDS (Table 8). The soils of the Kebir West were subject to large salts loss, reaching 261 t km^{-2} yr^{-1}.The flooding event of February 2012 alone contributed to 50500 tons of salts, which represents 10% the annual load. Zit-Amba dam sub-catchment and the lower catchment have elevated soil degradation compared to Beni-Haroun dam.

In addition to the flooding loads contribution, table 8 gives fluxes, specific fluxes and retention rate of the dissolved nitrogen forms. Zit Amba dam received 282 t yr^{-1} of TDN of which 76 t yr^{-1} was provided during the flooding event of late February 2012. The amount of NH_4 contributed to 18%, NO_3 49% and the DON to 28%. The dam received annually 204 tons of DIN but removed 57% of that amount. Among the DIN forms, N-NH_4 was weakly retained (33%) but N-NO_3 experienced large removal within the dam (66%). Moreover, because of the dam endogenous transformations (removal of NO_3 and NH_4 as nutrients for phytoplankton), Yet, all the Redfield ratios have been deeply changed and sharply decreased, indicating the great dam effects on the nutrients biogeochemical cycles. Fortunately, before reaching the sea (at the stream's mouth) the water quality in term of Redfield loading ratios were improved.

The TDP and P-PO_4 budget of the dam seems to be balanced as the entrance equals the exit deliveries. However, the DOP had a positive budget as shown in table 8. The P-PO_4 flux was enhanced at the KW-M owing to the large input from the lower basin area. The P-PO_4 specific flux was however low, not exceeding 11 kg km^{-2} y^{-1}.

Similarly, the DOP masses increased at the stream's mouth with large specific loss reaching 45 kg km^{-2} y^{-1}. On the whole, TDP flux and yield was relevant over the catchment and can result in some large anthropogenic inputs over the lower catchment (Table 8).

Table 8: fluxes of water, sediment (TSS), salts (TDS), dissolved nutrients and particulate matter (t yr^{-1}) from and into Zit Amba dam and at the stream's mouth during 2012. The contribution of the flood event of February 2012 is also indicated. ZA-O: opening Zit Amba dam; ZA-E: exit Zit Amba dam; KW-M: Kebir West stream's mouth; Q: water volume. Negative values (-) denote retention rate and positive ones (+) denote release.

	Zit Amba dam						Kebir West stream		
	ZA-O (t yr^{-1})	Flood (t yr^{-1})	ZA-E (t yr^{-1})	Flood (t yr^{-1})	R/P (%)	Flood R/P (%)	KW-M (t yr^{-1})	Flood (t yr^{-1})	Yield (kg km^{-2} yr^{-1})
Q (10^6 m^3)	272	72	264	46	-3	-36	466	202	
NH_4	51	13	34	5	-33	-61	79	31	42
NO_2	16	5	7	2	-56	-60	18	7	9
NO_3	137	36	47	19	-66	-47	157	66	83
DIN	204	53	88	26	-57	-51	254	104	134
DON	78	23	72	21	-8	-9	99	38	52
TDN	282	76	160	47	-43	-25	353	142	186
PO_4	12	4	11	1	-8	-75	20	6	11
TDP	44	16	47	12	+7	-25	114	75	60
DIP	21	6	15	3	-29	-50	29	10	15
DOP	23	10.2	30	9.1	+30	+11	85	66	45
$Si(OH)_4$	694	166	422	100	-39	-40	1086	484	572
BSi	20		21		+5		17		9
POC1	181		625		+245		440		232
POC2	162		669		+312		512		269
POCt	309		1294		+319		951		501
TSS (10^3)	14	6	6	3	-57	-50	30.5	21.5	16053
TDS (10^3)	134.5	20	104	10	-23	-50	496	50.5	261053
POCt/TSS	2.2		10				3		
N:P	17		7				13		
Si:N	28		5				4		
Si:P	58		32				54		

The dam received 694 t yr^{-1} of Si-$Si(OH)_4$ from which 24% was brought during the flood event of late February 2012 (Table 8). The Silicate amount delivered by the dam has been more than doubled (1086 t yr^{-1}) when reaching the KW stream's mouth owing to the other minor tributaries inputs. This mass corresponds to high specific flux or yield, amounting 572 kg km^{-2} y^{-1}. Compared to the dissolved form the particulate Silica (BSi) was weakly represented. The $Si(OH)_4$: BSi ratio for waters entering and leaving the dam was only in the order of 35%. This may indicate that the strong part of silica has been stored in the dam. The delivered mass from KW-M was also not relevant compared to the dissolved silica (BSi: $Si(OH)_4$: 17/1088 = 1.5%).

The incoming flux of POC for Zit Amba dam was in order of 300 t yr^{-1}, with nearly equal amount of POC1 and POC2 (Table 8). However, the dam produces high masses of POC: 606 t yr^{-1} for POCt; 287 t yr^{-1} for POC1, as shown in table 8.

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CHAPTER V

CHAPTER V: VARIATION OF WATER DISCHARGE, PARTICULATE MATTER AND NUTRIENTS CONCENTRATION OVER THE SAF-SAF CATCHMENT

1. Biogeochemical features at the entrance and exit of Zerdaza dam and at Saf-Saf stream's mouth

At the Saf-Saf stream's mouth (SF-M), the water flow was highly variable, ranging from 1-11 $m^3 s^{-1}$ for the dry period and reached a maximum of 49 $m^3 s^{-1}$ during the flood event of February 2012 (Figure 22). The annual average was in the order 13.1±3.2 $m^3 s^{-1}$ (Table 9). Zerdaza dam received high variable discharge (0.7-34 $m^3 s^{-1}$) with an average of 10.1 $m^3 s^{-1}$ during the study period (Figure 22; Table 9). It delivered however half the received flow rate at its exit, as a result of water retention within the dam itself (Table 9). The inflowing water was weakly charged with TDS (217 and 739 mg L^{-1}) with an average of 367 mg L^{-1} during the study period as shown in Figure 22 and table 9. The lowest value (217 mg L^{-1}) was recorded during the stream flooding of February 2012 (Figure 22).

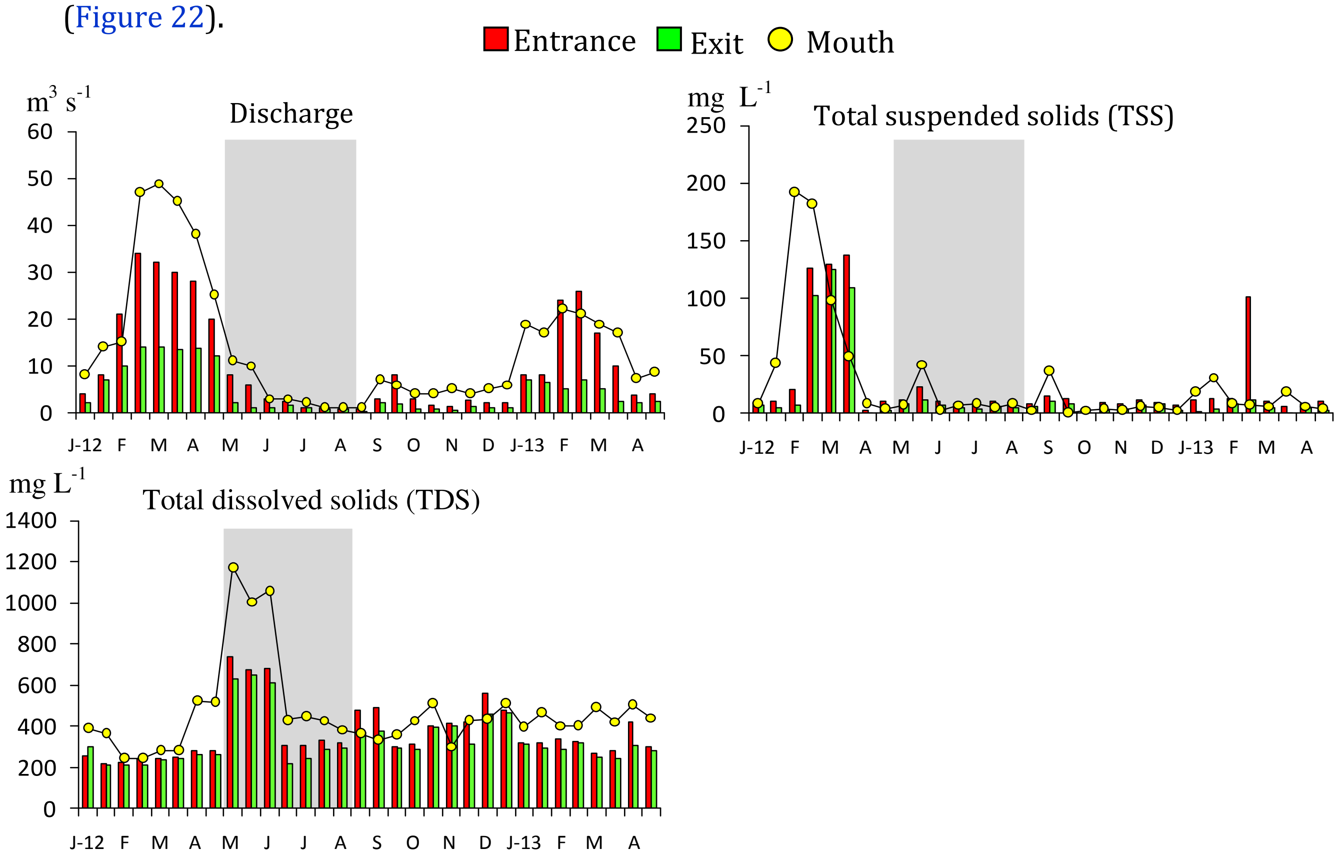

Figure 22: seasonal variations in hydrological parameters over the Saf-Saf catchment during the study period, January 2012- April 2013.

TDS concentrations at the dam's exit were regularly just comparable to the entrance's one (Figure 22; Table 9), since the dam is being mostly silted, and function then like a river. Similarly, the TSS levels at the entrance of Zerdaza dam varied in a large range (2-337 mg L^{-1}), with an average of 49 mg L^{-1} during the study period (Figure 22; Table 10). During the dry period the average concentration decreased to 11 mg L^{-1}. Also, because of the advanced silting the TSS removal by the dam was only in the order of 30 % (Tables 9; 10).

Table 9: hydrological and biogeochemical parameters (mean ± standard error) at the entrance and exit of Zerdaza dam and at the Saf-Saf stream's mouth, for the annual cycle January-December 2012. Mean values of particulate materials (BSi and POC) have been computed for the period March 2012-February 2013. Rr is the reduction rate of a given parameter by Zerdaza dam. Positive Rr indicated a release.

	Zerdaza dam						Saf-Saf stream	
	Opening		Exit		Rr (%)	Rr* (%)	mouth	
	2012	2013*	2012	2013*	2012	2013*	2012*	2013*
Discharge	9.3±2.3	12.6±3.1	4±1.1	4.6±0.8	-57	-63	13.1±3.2	16.3±1.9
TSS	50.3±22.1	46.4 ±11	44.5±21.2	5.5±1.4	-8	-88	122.7 ±48	126.3 ±3.3
TDS	383 ±31.5	321±46.5	342 ±10.2	286 ±10.2	-11	-7	476 ±50.6	440 ±14.8
TDN	58.8±5.3	72.7±9.9	56± 5.3	72.3±8.2	-5	-1	65.9±7.2	60.8±8.1
DIN	42.6 ±4.4	44.6±8.5	31.3±3.6	30.5±6	-27	-32	52.5±6.4	45.6±9.4
DON	16.5±2.6	28.2±3.1	22.9±3.3	41.7±4.5	+39	+48	13.9±3.1	15.3±3
NH_4	18.8 ±2.2	12.3±1.1	14.1±2.1	8.8±1.1	-25	-27	21.4±3.3	17.1±1.6
NO_3	22.5±3.8	30.5±8.1	16.5±3	20.5±6.2	-27	-33	27.4±5.2	26.5±9.1
NO_2	1.6±0.2	1.8±0.3	1.1±0.2	1.2±0.2	-31	-33	3.6±0.6	2±0.5
TDP	4.8±0.6	4.9±0.3	5.2±0.6	5.1±0.5	+8	+4	5.4±0.8	5.9±0.7
DIP	0.8±0.1	0.9±0.2	0.5±0.1	0.6±0.1	-38	-33	0.8±0.2	1 ±0.3
DOP	2.7±0.5	2.2±0.3	3.4±0.7	3.2±0.7	+26	+55	2.9±0.7	3.5±0.7
PO_4	1.8±0.3	2.1±0.4	1.4±0.2	1.4±0.4	-22	-33	2±0.5	1.9±0.4
$Si(OH)_4$	73±4.9	77.8±5.1	59.8±4	62.6±3	-18	-20	59.7±3.6	68.4±5
BSi	2.3±0.2	3.9±0.2	3.1±0.3	5.3±0.2	+35	+36	2.8±0.4	5.4±0.9
POC 1	1.8±0.2	2.5±0.4	2.1±0.2	3.3±0.3	+17	+32	1.9±0.2	3.2±0.2
POC 2	2.1±0.2	3.7±0.2	2.7±0.3	4.4±0.2	+29	+19	2.9±0.2	3±0.4
POC t	3.7± 0.4	6.2±0.6	4.8 ±0.5	7.7±0.5	+30	+24	8.5±0.9	13.9±1.1
N:P	24	21	22	22			26	24
Si:N	1.71	17	43	2.05			1	1.5
Si:P	41	37	43	45			30	36

The incoming water of Zerdaza dam showed high levels of TDN (20.5-107 µmol L^{-1}) with an average of 58.8±5.3 µmol L^{-1} (Figure 23; Table 9). Within the TDN pool, the DON fraction contributed to 28% and that of DIN was 72% (Table 10). Levels of DON fluctuated between 6.8 and 63.9 µmol L^{-1} with a average annual of 16.5± 2.6 µmol L^{-1} (Table 9), and those of DIN have largely fluctuated during seasons with an annual average of 42.6±4.4 µmol L^{-1}. During the wet period levels of NO_3 increased to 27.4 µmol L^{-1} forming 42% of TDN.

At Saf-Saf stream's mouth, the TDN concentrations varied between 17 and 141 µmol L^{-1} with an average of 65 µmol L^{-1} (Table 9). The DIN was the major component (78%) in which 51 µmol L^{-1}) when compared to those found behind Zit Amba dam (Table 10). NH_4 represents 31% and NO_3 42%. The delivered waters through the Saf-Saf stream's mouth have low values of DON (14 µmol L^{-1})

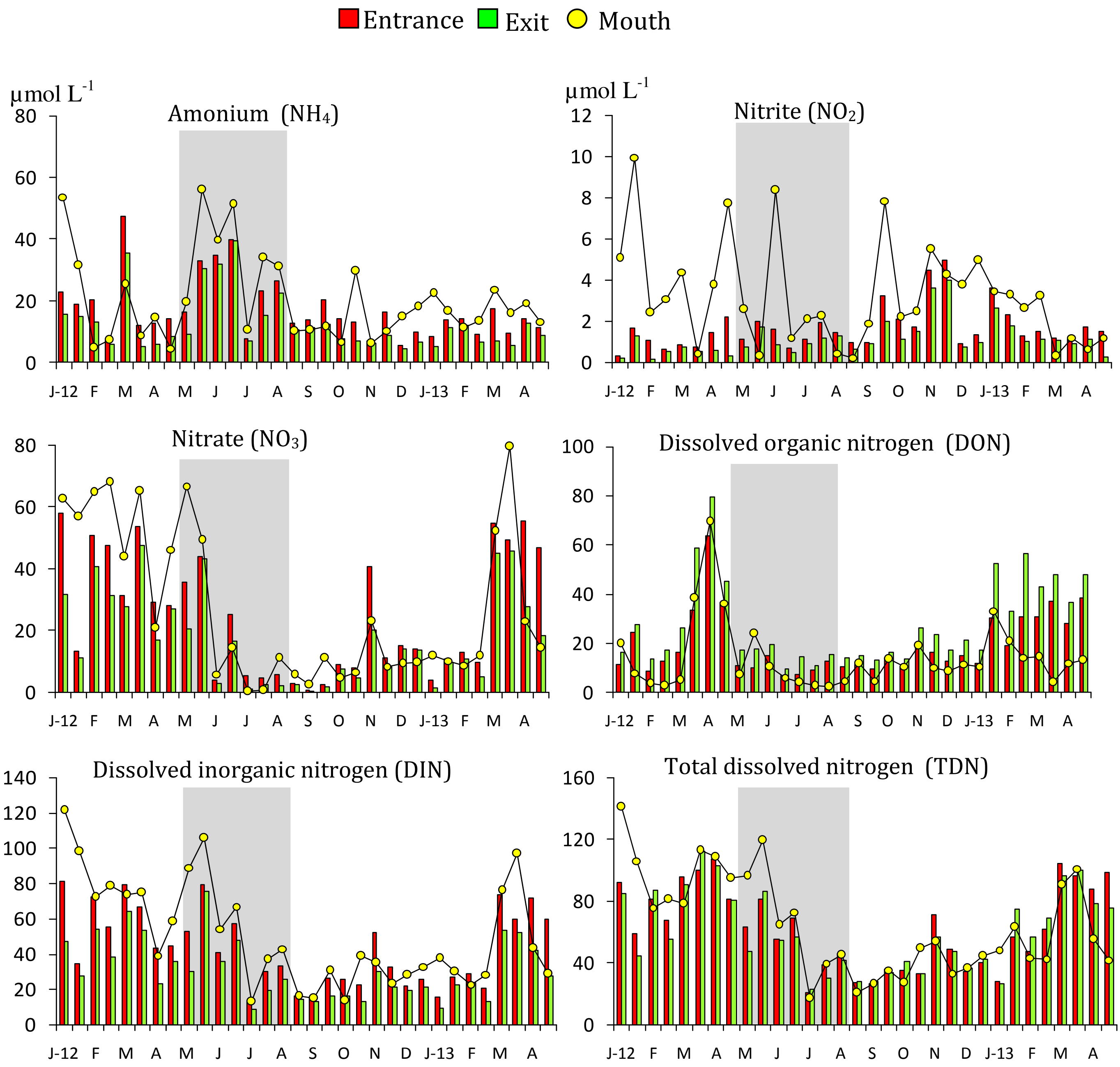

Figure 23: seasonal variations in the different forms of nitrogen over the Saf-Saf catchment during the study period, January 2012- April 2013.

At the entrance of the dam, TDP values varied between 1.3-11.7 µmol L^{-1} with a mean of 4.8 µmol L^{-1} during the study period (Table 9). The fraction of PO_4 presented 39% of TDP, with an average level of 1.8 µmol L^{-1} (Table 9). However, the DOP amount is still elevated throughout the study period with an average of 2.59 µmol L^{-1}, and contributed to 54% of TDP. The dam reduced however its leaving water levels of PO_4 and NH_4 by 28% and 25%, respectively (Tables 9; 10). This is because of the rapid dam's water renewing. Unlike the inorganic nutrient, mean levels of DOP (3.35 µmol L^{-1}) and DON (27.6 µmol L^{-1}) increased at the dam's exit and were released at rate of 42 % for DON and 25% for DOP (Figure 24; Tables 9; 10).

As shown in figure 23, the discharged waters via Saf-Saf stream's mouth were heavily charged with TDP (5.5 µmol L^{-1}), and ranged between 1.37 and 13.42 µmol L^{-1}. Within the TDP, the DOP and PO_4 represented 55% and 35%, respectively. Concentrations of PO_4 was not high (2 µmol L^{-1}) compared to the streams' mouths.

The $Si(OH)_4$ levels of the inflowing water were not high 74 µmol L^{-1} as well as for the waters leaving the dam (Table 9). The $Si(OH)_4$ reduction rate was not important, only in the order of 18% (Tables 9; 10). This behavior is related to the configuration of the dam become excessively silted and quickly renewed, thus not allowing sufficient residence time to eliminate this element. Indeed, of the 74 µmol L^{-1} received, the dam kept only a small amount and let pass relatively rich water in $Si(OH)_4$ (60 µmol L^{-1}), as shown in table 9 and figure 24 during the study period. When reaching the Saf-Saf stream's mouth levels of $Si(OH)_4$ slightly increased to 62±3.05 µmol L^{-1} . Levels $Si(OH)_4$ have however largely fluctuated between (31 and 95 µmol L^{-1}) and showed the lowest values (55 µmol L^{-1}) during the dry period.

The Redfield ratios were not significantly far from the balanced values: NO_3:PO_4 =14; DON:DOP =5; DIN:PO_4 =26; Si:N averaged =1 and Si:P =30 (Table 9).

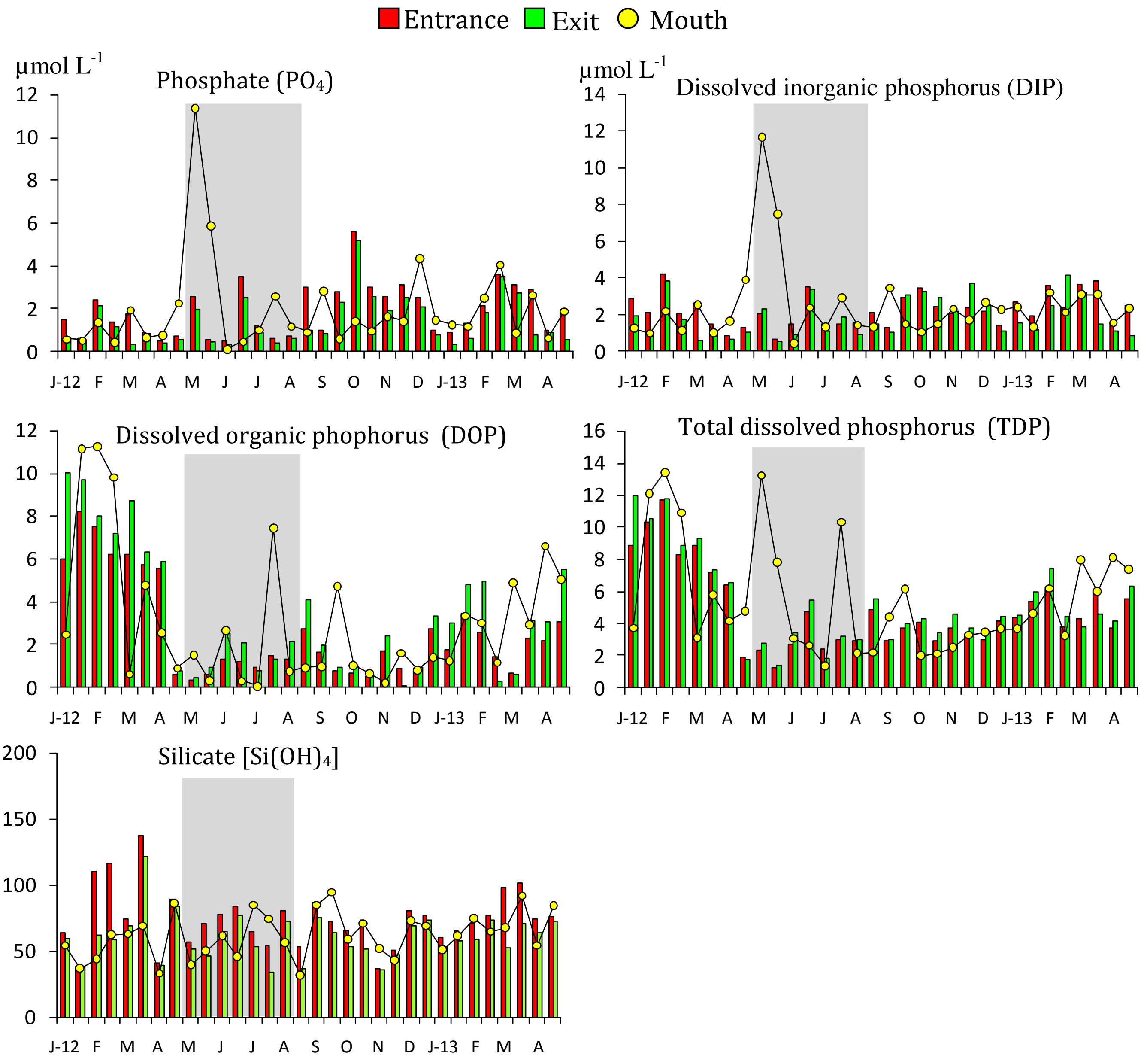

Figure 24: seasonal variations in the different forms of phosphorus and silicate over the Saf-Saf catchment during the study period, January 2012- April 2013.

Levels of particulate organic carbon introduced into the Zardaza dam showed the same trend as for Beni-Haroun and Zit Amba dams. The POCt levels followed a seasonal cycle with low values during the dry period (2.9 mg L^{-1}) and a maximum encountered during the wet period (4.6 mg L^{-1}), as can be seen in figure 25 . The annual average level was 3.7± 0.4 mg L^{-1} (Table 9). The fraction of POC1 contributed to 45% (1.8 mg L^{-1}) and that of the POC2 represented 55 % (2.6 mg L^{-1}) of POCt (Table 9).

Table 10: monthly reduction rate or release (%) of the various biogeochemical variables at Zerdaza dam during the study period, January 2012-April 2013. Negative values denote reduction and positive ones denote release.

	NH_4	NO_3	NO_2	DIN	DON	TDN	PO_4	DIP	DOP	TDP	$Si(OH)_4$	BSi	POC 1	POC 2	POCt	TSS	TDS
Ja-12	-32	-46	-31	-42	+46	-31	-60	-33	+48	+35	-7					-19	18
	-21	-16	-23	-19	+14	-5	-10	-58	+4	+2	-2					-50	-2
Feb	-35	-20	-89	-25	+58	-17	-11	-9	+1	+1	-44					-64	-5
	-18	-34	-12	-31	+40	-18	-17	-15	+11	+8	-50					-18	-14
Mar	-25	-12	-14	-19	+61	-6	-80	-78	+20	+5	-8	+92	+25	+50	+42	-3	-2
	-55	-12	-32	-20	+76	+12	-7	-32	+6	+2	-11	+68	+56	+67	+100	-20	-4
Apr	-54	-42	-60	-46	+25	-4	-19	-21	+4	+3	-4	+7	+78	+100	+91	-50	-8
	-42	-4	-87	-20	+24	0	-24	-23	+28	+8	-5	+9	+29	+5	+14	-73	-6
May	-44	-43	-35	-43	+60	-25	-24	-23	+89	+17	-9	+17	+15	+13	+14	-25	-15
	-8	-2	-13	-5	+75	+4	-17	-39	+25	+13	-35	+60	+77	+50	+95	-44	-4
Jun	-8	-34	-49	-12	+31	-1	-32	-25	+47	+24	-17	+15	+63	+36	+47	-22	-11
	-1	-34	-34	-17	+38	-11	-28	-28	+53	+16	-7	+59	+97	+51	+38	-27	-28
July	-11	-81	-19	-33	+99	13	-25	-26	+81	+26	-17	+31	+31	+25	+27	-53	-20
	-17	-43	-38	-36	+22	-22	-35	-44	+2	+8	-38	+27	+44	+25	+32	-42	-13
Aug	-34	-61	-11	-23	+22	-10	-16	-65	+11	+4	-9	+24	+109	+40	+68	-44	-8
	-15	-9	-32	-15	+35	+4	-68	-21	+72	+14	-32	+9	+82	+54	+80	-16	-23
Sep	-17	-25	-5	-17	+31	+4	-18	-22	+2	+3	-13	+41	+50	+30	+39	-23	-23
	-38	-26	-38	-37	+40	-17	-18	-11	+42	+8	-12	+43	+13	+82	+41	-25	-3
Oct	-46	-17	-46	-36	+16	-18	-8	-19	+45	+5	-18	+15	+16	+21	+19	-67	-8
	-45	-42	-12	-42	+33	-19	-14	-29	+79	+18	-30	+19	+15	+20	+18	-65	-1
Nov	-11	-50	-20	-42	+38	-21	-27	-16	+59	+23	-2	+23	+17	+25	+21	-45	-3
	-46	-27	-20	-35	+45	-9	-19	-22	+81	+15	-6	+22	+76	+48	+59	-29	-25
Dec	-16	-8	-18	-11	+37	+7	-18	-11	+59	+15	-14	+59	+18	+17	+17	-4	-18
	-35	-3	-30	-17	+44	+5	-21	-19	+12	+7	-5	+44	+11	+9	+10	-55	-3
Ja-13	-38	-60	-27	-41	+44	-4	-64	-42	+23	+3	-11	+30	+3	+13	+7	-78	-2
	-18	-11	-23	-16	+73	+31	-55	-41	+21	+10	-12	+74	+100	+10	+33	-64	-8
Feb	-15	-15	-24	-16	+74	+20	-15	-30	+43	+21	-18	+71	+56	+16	+30	-23	-15
	-27	-49	-25	-37	+85	+36	-4	-5	+47	+17	-4	+6	+100	+29	+45	-87	-1
Mar	-59	-18	-12	-27	+40	-8	-12	-13	+47	+14	-46	+13	+28	+13	+19	-47	-6
	-40	-7	-17	-13	+30	+3	-74	-62	+74	+11	-30	+52	+15	+26	+22	-78	-15
Apr	-11	-50	-36	-42	+29	-22	-15	-30	+21	+11	-14	+20	+33	+31	+32	-30	-27
	-22	-61	-83	-54	+25	-23	-73	-67	+31	+14	-5	+31	+17	+28	+23	-73	-7

Levels of BSi of waters entering the dam had largely varied throughout the seasons (0.37-4.66 µmol L^{-1}), with an average of 2.7 µmol L^{-1} (Table 9). Levels decreased to 1.6 µmol L^{-1} during the dry period. At the dam's exit concentrations of BSi increased two-fold the values of the incoming waters (Table 9). All the particulate organic forms experienced large production within the dam in particular for the POC1, POC2 and BSi which have approximately increased by 32, 26 to 35%, respectively (Table 10). At the dam exit the BSi concentration increased to 3.7 µmol L^{-1} (Figure 25).

Particulate organic carbon at Saf-Saf stream's mouth showed no clear seasonal cycle (Figure 25). POCt levels varied from 1.4-18.6 mg L^{-1} with an average of 10 mg L^{-1}. As for waters entering and leaving the dam, POC2 was the major component of the total particulate organic carbon (Table 9). Concentrations of BSi at the stream's mouth fluctuated between 0.21 to 9.22 µmol L^{-1} with an average value of 3.5 µmol L^{-1}.

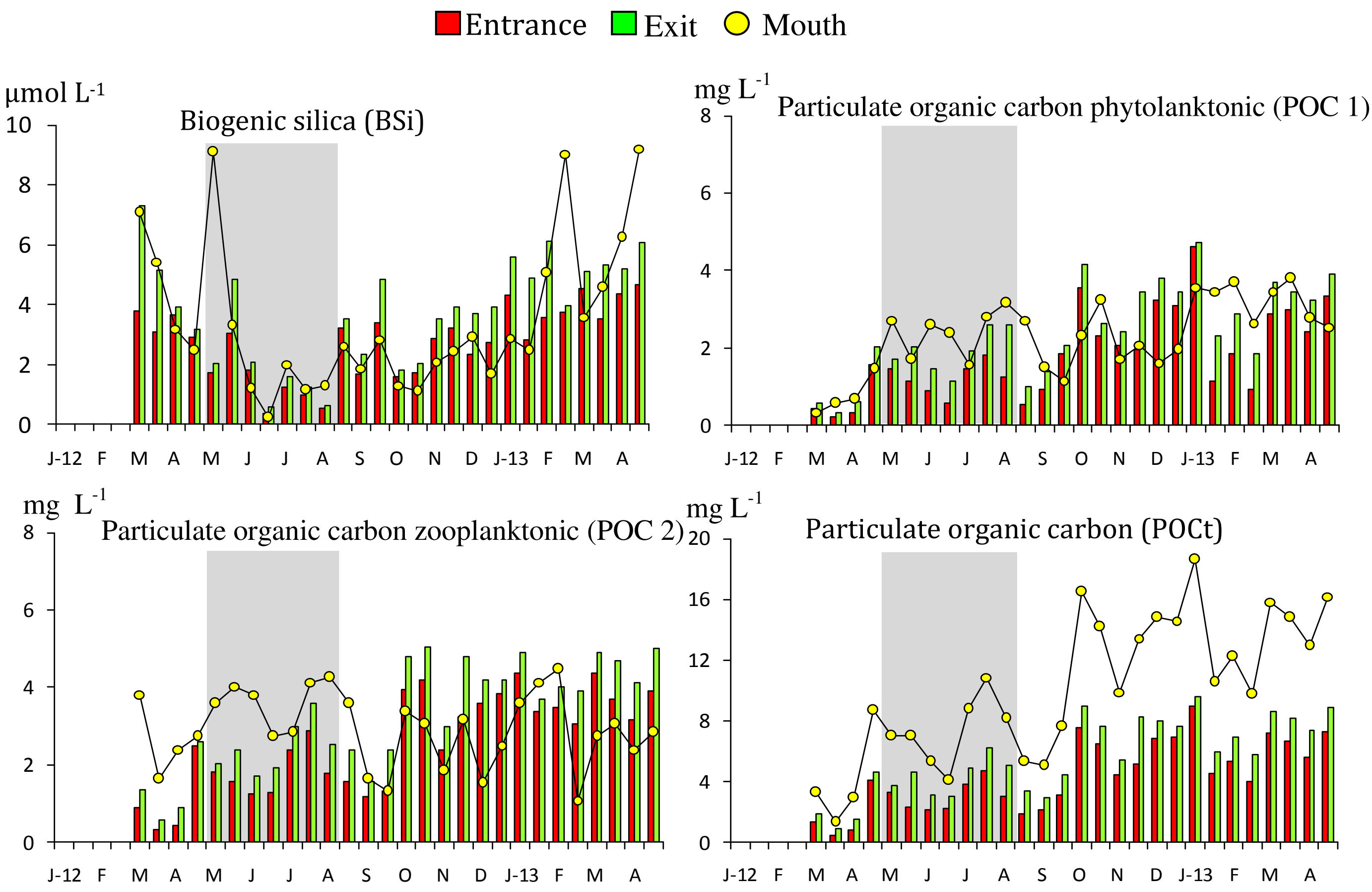

Figure 25: seasonal variations in biogenic silica and particulate organic matter over the Saf-Saf catchment during the study period, January 2012- April 2013.

2. *Fluxes of water TDS, TDS, dissolved nutrients and particulate matter at the entrance and exit of Zerdaza dam and at Saf-Saf stream's mouth*

Table 11 provides the annual fluxes of the various hydrological and biogeochemical parameters. Zardaza dam has received during 2012 about 290 10^6 m^3 from which half volume was retained in. The flood of February only contributed to 25 % the inflowing water amount.

During the same period the Saf-Saf stream discharged into the sea 408 10^6 m^3 yr^{-1} (Table 11) of which 20 % was delivered over the flood of February 2012. In parallel, the receiving water brought into the Zardaza dam 44000 tons of suspended sediment, most of which (40%) was delivered behind the dam (Table 11). Since the flood of February was heavily charged with suspended sediment, it has brought strong masses of sediment contributing to about third the annual load. A strong sediment mass (121000 t yr^{-1}) was delivered into the sea during 2012, of which about 40% was brought during the flood event. The specific erosion in terms of sediment (or soil sediment loss) over the catchment reached 105 t km^{-2} yr^{-1} (Table 11). The dam also received annually 87500 tons of TDS (Table 11), from which 59 % was trapped. The Saf-Saf annually delivered strong masses of TDS into the sea (1667000 tons). This corresponds to a specific flux of 1440 kg km^{-2} yr^{-1} over the catchment, as reported in table 11.

As shown in table 11 Zezdaza dam received large load of TDN, most of which was in the form of DIN. The DON only contributed to third the incoming load. However after crossing the dam, the TDN compounds have been modified, where the DON load behind the dam slightly decreased, but the DIN one heavily decreased. The DIN form has experienced large retention, and its load was reduced at about 66%. Among the DIN pool both NH_4 and NO_3 were heavily removed by the dam at a rate of 69 % and 65 %, respectively. The flood of February 2012 brought however much more N-NO_3 (46 tons) than N-NH_4 (11 tons). About third these masses has been trapped within the dam. The DON flood load was low and sensibly comparable to that of NH_4, but it was not much retained within the dam, as the phytoplankton uses preferably inorganic nutrients instead of the organic form (Table 11). The specific load was high both for inorganic and organic nitrogen forms. It reached 225 kg km^{-2} yr^{-1} for DIN and 108 kg km^{-2} yr^{-1} for DON.

The TDP fluxes entering and leaving Zerdaza dam were nearly equal, because of the high DOP contribution. The DOP has even been retained by the dam (Table 11), while not only did P-PO_4 input was low but was also largely retained (69%). Additionally, as can be seen in table 11, the flood of February alone has brought third the annual load of DOP.

When reaching the stream's mouth, loads of TDP increased to 98 t yr^{-1} (37%), due to the agricultural and household inputs from the lower catchment. The corresponding yield reached then 85 kg km^{-2} yr^{-1}. P-PO_4 flux also increased in same magnitude, with a specific flux of 19 kg km^{-2} yr^{-1}. When compared to the flux behind the dam, the contribution of P-PO_4 within the TDP pool increased to 22 % at Saf-Saf stream's mouth (Table 11).

Zerdaza dam has received a relevant masses of Si-$Si(OH)_4$, particularly during the flood event of February 2012 (Table 11). Most of this important load was however trapped by the dam. This removal increased to 77 % for the flood event. If compared to Si-$Si(OH)_4$ load behind the dam (257 t yr^{-1}), the delivery at the stream's mouth increased to 990 t yr^{-1}, from which 188 t yr^{-1} comes from the flood event of February 2012. The Si-$Si(OH)_4$ specific flux was highest among all of the nutrients, reaching 855 kg km^{-2} y^{-1} (Table 11).

Loads of BSi entering Zerdaza dam represented only 2.5 % of that of $Si(OH)_4$, but this fraction increased somewhat at the dam exit to reach 4.3 %, as can be deduced from table 11. The delivered BSi mass into the sea increased by more than 3-fold regarding its amount released from the dam.

Table 11: fluxes of water, sediment (TSS), salts (TDS), dissolved nutrients and particulate matter (t yr^{-1}) from and into Zerdaza dam and at the respective stream's mouth during 2012. The contribution of the flood event of February 2012 is also indicated Q: water volume. Negative values (-) denote retention rate and positive ones (+) denote release.

	Zerdaza dam						Saf-Saf stream		
	Opening (t yr^{-1})	Flood (t yr^{-1})	Exit (t yr^{-1})	Flood (t yr^{-1})	R/P (%)	Flood R/P (%)	Mouth (t yr^{-1})	Flood (t yr^{-1})	Yield (kg km^{-2} yr^{-1})
Q (10^6 m^3)	290	72	134	31	-54	-57	408	81	
NH_4	81	11	25	4	-69	-64	98	7	85
NO_2	5	1	1	0.2	-80	-80	22	3	19
NO_3	145	46	51	14	-65	-70	78	71	67
DIN	231	58	78	18	-66	-69	261	81	225
DON	100	10	68	6	-32	-40	125	3	108
TDN	330	68	146	25	-56	-63	386	84	333
PO_4	13	4	4	1	-69	-75	22	2	19
TDP	62	20	59	9	-5	-55	98	14	85
DIP	20	6	6	2	-70	-67	33	3	28
DOP	102	14	53	16	-48	+14	65	11	56
$Si(OH)_4$	715	213	257	49	-64	-77	990	188	855
BSi	18		11		-39		37		32
POC 1	188		111		-41		337		291
POC 2	263		158		-40		829		715
POCt	444		281		-37		1166		1413
TSS (10^3)	44	14	17.5	5.2	-60	-63	121	48	104500
TDS (10^3)	87.5	16	35.5	6	-59	-62	1667	18.2	1440000
POC t/TSS	1		1.6				1		
N:P	18		19.5				12		
Si:N	3		3.2				13		
Si:P	55		64				45		

Waters reaching the dam were strongly charged with POC. They have brought 444000 t yr^{-1}(Table 11) of POCt, in which the POC2 formed 60 %. However, this fraction was same trapped of POC1, which was removed at 40%. The POC delivery through the Saf-Saf stream's mouth was enormous, over 1.6 10^6 t yr^{-1}. The major load was in the form of large particles (POC2> 200µm). The POC specific flux varied according to the particle size: 291 t km^{-2} y^{-1} for POC1 (POC1< 200 µm) and 715 t km^{-2} y^{-1} for POC2 (POC2> 200 µm). The POC load represented only around 1 % the sediment one. More importantly is that the load of the dissolved salts (TDS) was 14-fold higher than that of the sediment delivered into the sea.

DISCUSSION

Discussion

Very little information is provided on the hydrology and chemistry of the eastern Algerian rivers and their adjacent coasts (Ounissi and Bouchareb, 2013; Aounallah, 2015; Taamallah et al., 2016).

All the nutrients undergo important biogeochemical transformations across their transfer within the aquatic continuum, from the upper to the lower catchment. Waters reaching the dams were heavily loaded with DIN and DIP. At the exit of the dams, their levels are substantially reduced, but enriched again during their transit to the sea, as a result of anthropogenic inputs over the lower catchment. This spatial distribution has been reported for the same catchments and dams by Bouchareb (2013). Also, Ounissi and Bouchareb (2013) demonstrated that not only theses dams can play a crucial role in trapping strong masses of sediments and salts but are also special sites for biogeochemical transformations of organic and inorganic nutrients. These are especially: retention of dissolved inorganic nutrients; production of dissolved organic matter; change in the balance of Redfield ratios (N/P/Si); oxidation of NH_4 to NO_3 (nitrification); modification of the biogeochemical cycles of N, P and Si; limitation of N, P and Si Sea fluxes; salt and sediment retention from upper catchment.

The specific fluxes of DIN were high, ranging from (42 to 225 kg km^{-2} yr^{-1}). These values can be considered to be among the highest in the Mediterranean rivers (Ludwig et al., 2009; Ounissi and Bouchareb, 2013; Ounissi et al., 2014; Aounallah, 2015).

It appears that dams act as real biogeochemical factories, transforming the received inorganic nutrients (DIN and DIP) into dissolved organic nutrients (DOP and DON). These organic nutrients are mainly produced by the metabolic activity of planktonic organisms (metabolic waste, lyses of microorganisms, decomposition of organic matter, Le Gal, 1989). In terms of concentrations, inorganic nutrients are retained in dams at retention rates varying between 25-51% for NH_4 and 19-34% for PO_4. For the same dams Ounissi and Bouchareb (2013) reported very high retention rates. The $Si(OH)_4$ masses entering the dams are retained (Ounissi and Bouchareb, 2013) in varying proportions between 18% in Zerdaza, 29% in Zit Amba and 20% in Beni-Haroun. These traps were lower than those of DIN (28-40%) and DIP (17-28%). It is important to emphasize that these retention rates are remarkably comparable in terms of concentrations with those of a dam under a semi-arid Mediterranean climate in

Australia (Cook et al., 2010), where PO_4 was retained at 77%, NO_3 at 92% and $Si(OH)_4$ at 39%. In the temperate reservoirs of the Marne, Seine and Aube, (Garnier et al., 1999), low NO_3 retention (40%) is observed but higher retentions (50%) were reported for $Si(OH)_4$ and for PO_4 (60%). According to Ludwig et al. (2009) also confirmed that the high specific fluxes of NO_3 are typical of the north Italian rivers. In the other temperate reservoir of Iron Gate I built on the Rhine River, Humborg et al. (2000) demonstrated that over 80% of dissolved Si reduction can be related to the retention by this dam.

Despite the ecological importance of DON in aquatic systems (Mortazavi et al., 2001; Seitzinger and Sanders, 1997; Wiegner et al., 2006), information on the spatial and temporal distribution of DON in dams is lacking. This study clearly shows that dams produced large amounts of DON (42-63%) and DOP (25-51%) in terms of concentration. The large inorganic nutrients amounts would partially be used to produce equivalent amounts in DON and DOP in the studied dams. Prasad and Ramanathan (2008) recorded comparable values reaching in average 6 µmol L^{-1} in a mangrove estuarine system under post monsoon and summer conditions. The other negative role of dams would be the modification of the loading Redfield ratios, changing from relative balanced values to high and altered ones. The delivered waters from the dam were highly disturbed in terms of Redfield ratios. According to the EEA (1999) report, very high N:P ratios are commonly encountered in the mouths of the Mediterranean rivers (Table 13).

Table 12: Average values of the N:P ratio in some Mediterranean Rivers (EEA, 1999). * Present study.

River	Ratio	Country
Rhône	33,53	France
Hérault	63,03	France
Ebre	181,46	Spain
Pô	55,31	Italy
Tever	12,17	Italy
Axios	1,05	Grèce
Akheloos	0,06	Grèce
Seyhen	7,18	Turkey
Seyhen	58,96	Turkey
Moulouya	35,47	Marocco
Mafrag	10-24	Algeria
Seybouse	90-135	Algeria
Kebir-Rhumel	17	Algeria*
Kebir West	23	Algeria*
Saf-Saf	26	Algeria*

At the lower catchment part, the increase of DIN and DIP may be mostly related to intensive agricultural activities spreading in this area of the SF, KW and KR streams. Despite the large losses of inorganic nutrients in the dams, there are significant additional inputs after the dams, up to the mouths. Despite the large inorganic nutrient losses in dams, they were additional inputs behind dams; the DIN rate was significant, varying from 32% in the KW to 28% in the SF and rate of DIP releases decreased by 24-40%. In contrast to N and P, derived mostly from anthropogenic inputs, $Si(OH)_4$ originated from rock weathering and entered streams mouths the dams, increased only in the range of 15–30% compared to their levels at dam exits. In terms of specific fluxes, the small catchments of KW and SF deliver to the sea large masses of $P–PO_4$ (11 to 19 kg km^{-2} yr^{-1}) in comparison to the large catchment of KR (4 kg km^{-2} yr^{-1}) that comprises the biggest dam of Algeria, these values have decreased compared to the values of the same streams according to Ounissi and Bouchareb (2013). The large amount of the DON that was introduced to coastal water (up to 247 t yr^{-1} equivalent 30 kg km^{-2} yr^{-1}) suggests that this fraction may contribute noticeably to marine eutrophication, as already demonstrated by Seitzinger and Sanders (1997).

The Si:N ratios were in more than 30% of the cases below the diatoms requirements (Redfield et al., 1963), implying that N was delivered in excess over silica (Si:N < 1). As has been revealed by Ounissi and Bouchareb (2013), the alteration of Si:N ratios become worldwide problematic for almost all world developed rivers; the Danube (Humborg et al., 2000), the Mississippi (Turner and Rabalais, 1991, 1994), the Po (Justicet al. 1995), Chesapeake Bay (Fisher et al., 1988, Correll et al., 2000).

However, BSi concentrations of the studied streams were very low (3 µmol L^{-1}) compared to the rivers worldwide (28 µmol L^{-1}) provided in the work of Conley, (1997). Although very high amount of POC characterize the studied dams, which represented for example 3 to 6-fold the mean concentration from the North Mediterranean Rivers (e.g., Bizsel et al., 2011; Cozzi et al., 2011; Higueras et al., 2014). The POC fluxes are consequently increased. The POC yield reached 215000, 501000 and 1413000 kg km^{-2}yr^{-1} for KR, KW and SF respectively deliveries and formed 1-3 % of the TSS amounts. The BSi yield was 5-32 kg km^{-2}yr^{-1} and represented only 0.3-0.5% of TSS.

The studied dams trap, about 56 to 95% of the received masses corresponding to 14000 to 238000 t yr^{-1}. According to Taamallah et al., (2016) Mexa and Chaffia dams retained 43-52% of the received sediment masses (371000 to 143000 t yr^{-1}), respectively. The transfer of total suspended sediments to the sea was about 30500-121000 t yr^{-1} depending on the catchment, which correspond to an erosion rate ranging from 14 t km^{-2} yr^{-1} for the KR catchment, to 16 t km^{-2} yr^{-1} for the KW and 104 t km^{-2} yr^{-1} for Saf-Saf (Table 14).

Table 13: Sediment yield (TSS, t km^{-2} yr^{-1}) for some Mediterranean and Algerian rivers and dams.

River/dam opening	t $km^{-2}yr^{-1}$	References
Mediterranean rivers	251	UNEP/MAP/MED POL (2003)
Ebro River, Spain	214	UNEP/MAP/MED POL (2003)
Têt stream, France	40	Serrat et al (2001)
Rhône River, France	324	Pont et al (2002)
Italian rivers	780	UNEP/MAP/MED POL (2003)
Greece rivers	1140	UNEP/MAP/MED POL (2003)
Albanian rivers	2780	UNEP/MAP/MED POL (2003)
North African catchments	800	Fox et al (1997)
Maghreb catchments	397	Probst et al (1992)
Majrda, Tunisia	963	UNEP/MAP/MED POL (2003)
Moulouya, Morocco	250	UNEP/MAP/MED POL (2003)
Nile, Egypt	42	UNEP/MAP/MED POL (2003)
Cheliff, Algeria	78	UNEP/MAP/MED POL (2003)
Isser, Algeria	193	UNEP/MAP/MED POL (2003)
Kebir west, Algeria	200	UNEP/MAP/MED POL (2003)
Seybouse, Algeria	333	UNEP/MAP/MED POL (2003)
Soummam, Algeria	513	UNEP/MAP/MED POL (2003)
Tafna, Algeria	143	UNEP/MAP/MED POL (2003)
Cheffia dam, Algeria	2700	Touaibia (2010)
Charf dam, Algeria	300	Touaibia (2010)
Beni-Haroun dam, Algeria	64	Bouchareb (2013)
Zit El-Amba dam, Algeria	374	Bouchareb (2013)
Zerdaza dam, Algeria	192	Bouchareb (2013)
Chaffia dam, Algeria	143	Taamalah et al (2016)
Mexa dam, Algeria	371	Taamalah et al (2016)
Mafragh catchment' outlet, Algeria	1974	Taamalah et al (2016)
Soummam River	28	Youcef and Amira (2017)
Isser River	52	Youcef and Amira (2017)
Sebaou River	59	Youcef and Amira (2017)
Kebir-Rhumel stream	14	Present study
Kebir West stream	16	Present study
Saf-Saf stream	104	Present study

Except for Saf-Saf catchment, the sediment loss over the two other studied catchments was sensibly lower than those of Mediterranean rivers (60 t km^{-2} yr^{-1}, Meybeck et al., 2007). In the same context, the waters of the dams are salinized (in terms of TDS) annually at the rate of 87500 to 687000 tons, while marine waters receive between 351000 and 1667000 tons of continental salts. The dams of Chaffia and Mexa received annually 47000-148000 tons of dissolved solids, from which 21-61% is trapped; the Mafragh estuary outlet delivered annually to the sea 436000 tons of TDS (Taamallah et al., 2016). The soil of the basins undergoes another aspect of alteration in the form of loss of salts at a rate varying between 43 and 1440 t km^{-2} yr^{-1}. Salinization of both the dams and the soils of the catchments is not only due to the semi-arid climate at the top soils' catchments (subject to high evaporation), but also to chemical fertilizer inputs of agricultural origin. It is thus considered that all the catchments are at least somewhat affected in several ways: high levels of NH_4, PO_4, reduction of $Si(OH)_4$, level, imbalance of Si:N:P ratios, high retention rate within dams, soil erosions and salinization and low nutrient inputs into the sea.

CONCLUSIONS

Kebir West (Ben Azzouz)

Conclusions

- The three studied catchments were characterized by high levels of NH_4 and PO_4, although at their upper part, when the headwaters enter the dams.
- The dissolved nutrient levels experienced considerable retention in dams, constantly exceeding 50%, but they increased over the lower catchment, at the streams' mouths, owing to the human activities input.
- But $Si(OH)_4$ which is of natural origin, was low and experienced further removal behind the dams.
- Due to their trapping in dams, the nutrient fluxes into the sea have been significantly reduced, and remain in the order of a few hundred tons per year for DIN and a few thousand for $Si(OH)_4$.
- More importantly is the large production of organic matter by the dams both as dissolved (DON, DOP) and either as particulate form (POC, BSi).
- But this is not so evident for their fluxes behind dams because the stream flow is reduced by 46-83% after crossing the dams.
- In terms of levels, the POC and BSi were released by the dams at large rates (30-60%), in contrast to the sediment amounts which were heavily removed at 57-95%.
- The sediment loss over the catchment area was reduced (14 and 104 t Km^{-2} yr^{-1}, depending on the dam), due to the dams retention, but the salts' soil loss is still more important.
- About third the annual water discharge, sediment, salt and nutrient loads was brought during the flood event of late February 2012.
- Overall, these hydrological and biogeochemical features could impact the stream systems and their neighboring coasts.

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ANNEX

The methods of analysis

Ammonium Nitrogen (NH_4^+ + NH_3) analysis
Principle:

In slightly basic medium, the ammonium form a monochloramine with dichloroisocyanurique acid.The latter reacts with phenol to form an indophenol a blue colored compound whose intensity is proportional to the concentration of ammonium. The reaction is accelerated by the nitroprusside. This measurement technique has been applied for the determination of low concentrations where the error remains below 5%.

Reagents:

Reagent 1: Phenol-nitroprusside solution.
Dissolve cold: 3.5 g of phenol and 40 mg of nitroprusside sodium in 100 ml of water distilled. This reagent is stable after a few weeks in a cold, dark place.
Reagent 2: Dichloroisocyanurate solution.
Dissolve cold: 28 g of trisodium citrate, 500 mg of dichloroisicyanurate and 1.4 g of soda in 100 ml of distilled water. This reagent preserves in the fridge for 1-2 months.
Dosage or Assay:
A standard gamut must be made first followed by addition in a spectrophotometer tub:
2 ml of reagent 1,100 ml ± 1 ml of sample or standard,2 ml of reagent 2. After 8 hours of waiting in the dark, the absorbance is read with a spectrophotometer at 630 nm.
Concentrations are determined using the standard gamut, with the linear equation:

$$Do = aC+b.$$

Do: is the optical density.
C :is the concentration.
a :is the slope = 0.0166; b: the ordered originally = 0.0223; R^2 *(0.9982)the coefficient of determination measuring the quality of the adjustment of the right to the pairs of points of the cloud Do and C.*

Nitrate (NO_3) analysis
Principle:
The sample, stamped by a solution of ammonium chloride, move in a column of cadmium processed copper which serves to reduce nitrates into nitrites.It is thus the sum of the nitrite present in the sample over those formed by the reduction of nitrates which is measured using the same reagents than stated in the dosage of nitrites.The percentage of error with this method is less than 10%.
Reagents:
Reagent 1: Sulfanilamide solution.
Dissolve cold: 2.5 g of sulfanilamide with 13 ml of concentrated HCl and 250 ml water distilled.
Reagent 2: N-Dihydronaphthyl-1-ethylene diamine solution.
Dissolve cold: as many milligrams of N-Dihydronaphthyl-1-ethylene diamine as milliliters of distilled water. This solution is unstable and cannot be preserved for a long time.
Reagent 3: ammonium chloride solution.
Dissolve cold solution of ammonium chloride: 10 g of NH_4Cl in 1 L of distilled water.
Dosage or Assay:

A standard gamut must be made in advance. The sample or standard is injected into aloop, previously rinsed by the sample or the standard, and connected to the circuit via a valve system.
The absorbance is measured continuously by a spectrophotometer at 543nm wavelength.
The maximum absorbance are observed and concentrations are determined using the curve
Adjustment, the linear equation: **DO = *aC + b.*** a= 0.0429, b= 0.022 and R^2=0.9992.

Nitrites (NO_2) analysis
Principle:
In acidic medium (pH < 2), the nitrite ions form nitrous acid HNO_2 which reacts with of sulfanilamide to form a diazo complex. In the presence of N-Dihydronaphthyl-1-ethylene diamine forms a pink complex whose intensity is proportional to the concentration of nitrites. The percentage of error with this method is less than 5%.
Reagents:
Reagent 1: Sulfanilamide solution. Dissolve cold: 2.5 g of sulfanilamide with 13 ml of concentrated HCl and 250 ml water distilled.
Reagent 2: N-Naphtyl-1-éthylène diamine solution.
Dissolve cold: as many milligrams of N-Dihydronaphthyl-1-ethylene diamine as milliliters of distilled water. This solution is unstable and cannot be preserved for a long time.
Dosage or assay:
A standard gamut must be made in advance. Then, in a tub for spectrophotometer, we add:
1 ml of reagent 1, 50 ml sample or standard, 8 minutes of waiting, 1 ml of reagent 2, After 15 minutes of waiting, the absorbance is read with a 543 nm spectrophotometer.
Concentrations are determined using the standard gamut, the equation linear Do = aC + b where a = 0. 0421, b = 0.0237, and R^2 = 0. 9959.

Dissolved organic nitrogen (DON) analysis
Reagents:
Buffer solution:
-75 g of NH_4Cl in 400 ml water distilled,
- adjusted PH with NH_4OH up to 8.5.
-Complete with distilled water to 500 ml.
Oxidant Solution:
- 120 g NaOH in 2L of water distilled (A).
-Add 6 g of $K_2S_2O_8$ for every 100 ml of solution (A) to obtain the oxidizer.
-40 ml ED + 6 ml oxidant then Titrate with hydrochloric acid until the pH reaches the value between 2.6 and 3.2. The volume of added hydrochloric acid is X ml.
TDN= DON+DIN with **DIN = NO_3**
+ NO_2
+ NH_4
Dosage or Assay:
- 4 ml of the sample + 36 ED + 6 ml oxidant and heated 30 min more and allowed to cool
- The titration is made (X ml (200 ml HCl in 1,7L ED)
- 3 ml of the buffer solution is added.
- Pass by the column and recovered 25 ml.

- Was add 0.5 sulfanilamide and 0.5 NED.
- Spectrophotometer (543 nm).

Dissolved organic nitrogen concentrations are determined using the adjustment curve, the linear equation: **Do = aC + b**whose = 0.0429, b = 0.022 and R^2 = 0.9992.

Phosphates (PO_4^{-3}) analysis

The temperature of the samples must be between 15 and 30 c °. We proceed as follows:- prepare the reagent mixture.

-Measure 50 ml of sample.

-Add 5 ml of reagent mixture and mix immediately.

-Wait for 5 min and measure the absorbance at 885 nm in vats of 3 cm optical path, by contribution to distilled water.

Concentrations of phosphates are determined using the calibration curve, equation linear: 4Do**= aC + b** where a = 0.0227, b = 0.013 and R^2 = 0.9974.

The poly-phosphates (P_2O_6) analysis

Reagents

- Acid sulphuric 20 %(v/v)
- The mix - reagent.
- Solution of sodium hydroxide NaOH (40 g in a 500 ml of distilled water).

Procedure:

- Take 50 ml of water (sea water or waste water).
- Add 5 ml of sulfuric acid.
- Heat 30 min to a boil.
- Let cool.
- Adjust the pH to 2 with NaOH.
- Bring whether the volume to 50 ml with distilled water.
- Then perform the determination of polyphosphates on the solution obtained using the following method:

• Measure 50 ml of sample.
• Add 5 ml of the reagent-mixture.
• Wait 5 min and measure the absorbance at 885 nm.

Concentrations of phosphates are determined using the adjustment curve, linear equation:

Do = aC + b where a = 0.0227, b = 0.013 and R^2 = 0.9974.

Dissolved total phosphorus (TDP) analysis

Principle

The phosphate ions react with the molybdate to ammonium, in acidic medium and in the presence of antimony, to form a complex that is reduced by Ascorbic acid in blue complex. Formed Blue intensity is proportional to the concentration of phosphates and can therefore be measured using a spectrophotometer. The percentage of error with this method is less than 5%.

Reagents

- Perchloric acid d = 1.67 or sulfuric acid.
- Ascorbic acid 5% (5 g in 100 ml distilled water).
- Hydrochloric acid d = 1.16.
- The reagent-mixture: mixing the above reagents in the following proportions:
  - ✓ 50 ml potassium tartrate solution and antimony oxide (0.068 g in 50 ml of distilled water).
  - ✓ 100 ml of ammonium molybdate solution (3 g in 100 ml distilled water).

- ✓ 250 ml of sulfuric acid 2.5 $mol.l^{-1}$.
- ✓ 100 ml of ascorbic acid solution (10.5 g in 100 ml distilled water).

- NaOH sodium hydroxide solution (40 g in 500 ml of distilled water).

Procedure

- Add 50 ml of water in a flask (sea water or waste water)
- Then 3 ml perchloric acid,
- Heat (white fumes appear)
- Place a watch glass
- Heat 5 to 10 minutes,
- Remove the flask,
- Add 1 ml of ascorbic acid,
- Add 3 ml hydrochloric acid
- Put on the plate,
- Let cool,
- Adjust the pH to 7 with NaOH (N)
- Adjust the volume to 50 ml with distilled water,
- Then perform the determination of total phosphorus on the solution obtained using the following method:
    - Measure 50 mL of sample,
    - Add 5 ml of the reagent-mixture,
    - Wait 5 min and measure the absorbance at 885 nm from the base of 3 cm optical path.

Concentrations of phosphates are determined using the adjustment curve, linear equation:

$$\mathbf{Do = aC + b} \text{ where } a = 0.0227,\ b = 0.013 \text{ and } R^2 = 0.9974.$$

Organic phosphorus (POD) analysis:

Total and soluble phase phosphorus compounds of organic origin in the sample are obtained by difference between total phosphorus and the amount of phosphorus and orthophosphates the polyphosphates: DOP **= TDP – DIP with DIP = PO_4 + P_2O_5.**

Silicates Si $(OH)_4$ or SiO_4 analysis:

Principle

The heptamolybdate solution form with the dissolved silica (silicic acid) a silicomolybdique complex that gives, after reduction, an intense blue color. The percentage of error in continuous flow analysis is less than 1%.

Reagents

Ammonium molybdate Solution:

Dissolve hot (50 ° C): 20 g of nitrite of ammonium (NH4) 6Mo7O24H_2O in 500 ml of water distilled. Store away from light.

Solution of sulfuric acid to 4.5 M:

- R1: Mix 12 ml of (2) and 120 ml of (1) and make up to 500 ml with distilled water

This reagent must be freshly prepared daily.

- R2: Oxalic acid solution and sulfuric

Introduce 800 ml of distilled water in a flask, with 100 ml of concentrated sulfuric acid precaution.

-Add 30 g of oxalic acid ((COOH) 2, $2H_2O$) and make up to 1L.

-This reagent is stable for 1 month at room temperature.

Ascorbic acid solution:

Dissolve cold: $C_6H_8O_6$ 7.5 g ascorbic acid in 250 ml of distilled water

The signal drift in a salt gradient is 4% between freshwater and seawater.
Silicate concentrations are determined using the adjustment curve, the equation linear:

Do = aC + b where a = 0.0097, b = 0.008 and R^2 = 0. 9986.

Total suspended solids (TSS):

In terms of solid transport in suspension samples were filtered on filters Whatman GF/C (0.5 µm porosity), in order to retain all the higher size particles of 0,5- 1 µm filter is dried and weighed before and after filtration. The concentration is the result of the ratio between the weight differences of the filters to the corresponding filtered volume.

ARTICLE 1: Water and sediment retention in a reservoir (Zit Amba, Algeria)

Water and sediment retention in a reservoir (Zit Amba, Algeria)

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Abstract. This work assesses surface water, sediment and salts budget for Zit Amba dam (storage capacity 120 million m^3) in the Kebir West catchment (1 900 km^2; North Eastern Algeria), and the fluxes into the adjacent coast through the Kebir West river' outlet. The catchment is weakly populated with only 30 people km^{-2}, where the agricultural practices are becoming more intensive. The total suspended solids (TSS) and total dissolved solids (TDS) were measured twice a month during April 2012-March 2013 at the entrance and exit of the dam and at the River' outlet. Zit Amba dam seems to be affected by sediment sinking, and is thus submitted to severe and rapid clogging. The dam received annually about 9 000 tons of TSS and trapped an amount of 3 000 tons. This represented a retention rate of 67% of the receiving sediment masses. Annual retention of TDS in the dam is in the order of 100 000 tons (50%). The sediment yield reached a value of 20 t km^2 yr^{-1} for Zit Amba sub-basin. At the catchment outlet, the Kebir West outlet delivered 6 000 t yr^{-1} of TSS and 472 000 t yr^{-1} of TDS. This is equivalent to 4t km^2 yr^{-1} of sediment and over 325 t km^2 yr^{-1} of salt yield.
Key Words: catchment, Kebir West River, dam, sediment TSS, TDS.

Introduction. Rivers are the most important freshwater resource for humans. Social, economic and political development has, in the past, been largely related to the availability and distribution of fresh waters contained in riverine systems (Meybeck et al 1992). The rivers play a particular role in supporting the Mediterranean production whose most productive zones are limited at the adjacent coast (Friedl et al 2004; Teodoru et al 2006). Rivers play an important role in the global biogeochemical cycles by transferring dissolved and particulate substances from land to sea. By creating reservoirs in rivers, humans are substantially impacting the flux of sediments, organic matter and nutrients to the coastal zone (Vörösmarty et al 2003). To meet the growing water needs, numerous dams have been built all around the Mediterranean Sea (Lehner et al 2011). Changes in water quality of rivers due to the construction of dams have been recorded in literature (Petts 1984; Hart et al 1991). Dams may have a strong impact on the water and nutrient river discharge due to silicate (Si) and phosphorus (P) retention within sediments (Aviles & Niell 2007; Dürr et al 2011).

The climatic variability will increase, resulting in greater frequency and intensity of extreme weather events, which could increase, as a consequence of global climate change (Nunes & Seixas 2003; Nearing et al 2005). Soil erosion rates may be expected to change in response to changes in climate for a variety of reasons, the most direct of which is the change in the erosive power of rainfall (Favis-Mortlock & Savabi 1996; Williams et al 1996; Favis-Mortlock & Guerra 1999; Nearing 2001; Pruski & Nearing 2002). Soil erosion responds both to the total amount of rainfall and to differences in rainfall intensity, however, the dominant variable appears to be rainfall intensity and energy rather than rainfall amount alone (Nearing et al 2005). The changing precipitation pattern, and its impact on surface water resources, is an important climatic problem facing society today (De Luis et al 2000). This could be especially relevant in Mediterranean catchments where precipitation is characterized by scarcity, heavy spring and autumn storms, despite the large spatiotemporal variability (Ulbricha et al 2012). It has been reported that changes of water discharge and sediment load can cause various effects on river system itself as well as the estuary and coastal shelf environment (Zhang et al 2007). Chen (2000) pointed out that changes of river inputs (mainly water flow, sediment load as well as nutrient flux) to the oceans caused by river basin development, notably the construction of dams, have more subtle effects which go far beyond the delta and estuaries including the transformation of the coastal shelf ecosystem and the starvation of fish populations. The importance of fluvial sediment to the quality of aquatic and riparian systems is well established (Gray et al 2000). The sediment as the single most widespread cause of impairment of the Nation's rivers and streams, lakes, reservoirs, ponds, and estuaries were identified by Parry (1998) and Gray et al (2000). Rates of erosion are associated with climate, particularly the amount and intensity of rainfall, and can be modified by vegetative cover (Meybeck et al 1992). Rivers represent an important link between land and the ocean, and presently, they annually discharge about 35 000 km^3 of freshwater, and 22 109 tons of solid and dissolved materials to the ocean (Milliman & Farnsworth 2011). The transport of river borne sediment from the continental land mass to the world's oceans is a fundamental feature of the geology and biogeochemistry of our planet (Vörösmarty et al 2003).

Several studies (Milliman 1997; Walling 2006; Ludwig et al 2009) noticed that both water and sediment discharge of several world's rivers have shown progressive decrease during the last 50 years, which is more primarily due to reservoir construction, water abstraction, and soil conservation. Generally, the decrease of sediment load was reported (Zhang et al 2007) to coincide with decreasing trends of some major ions and total dissolved solids (TDS or salts).The dams are trapping a large portion of the sediments, which in turn may decrease the biological productivity as parts of nutrients are attached to the sediment (Taamallah et al 2016). In the Mediterranean basin, the information on water erosion is still scarce (Meybeck & Ragu 1996) and particularly lacking in Algeria coastal basins (Benblidia 2011; Remini 2010). The erosion rate of several Algerian dams had been however assessed by Touaibia (2010), but had not considered the amounts of sediment delivered from the dams' exits. In three dams belonging to North Eastern coastal catchments the sediment and salts budget had been however assessed by Bouchareb (2013). This work challenges to assess surface water, sediment and salts budget for Zit Amba dam in the Kebir West basin. The aim of this study is also to determine water, sediment and salts fluxes into the adjacent coast through the Kebir West catchment outlet.

Material and Method

Sampling site. Dam of Zit Amba (wilaya of Skikda) was recently built, knowing that this dam currently feeds the chief place of the wilaya as well as the daïra of Azzaba (Harrat & Achour 2011), that situated in Kebir West catchment occupied an area of 1 900 km^2 (Figure 1), but very weakly populated, with only 30 people km^{-2}. The downstream part of the basin of the reservoir is located in the wilaya of Skikda, the central and upstream parts are in the wilaya of Guelma (Harrat & Achour 2011). Zit Amba (120 million m^3 storage capacity) reservoir is used for irrigation and drinking water. Zit Amba reservoir is fed by two tributaries of Kebir West stream, with Oued El hammam at the south and Oued Mechekel at the west. Oued El hammam is submitted to some urban pollution sources and hydrothermal used water, but Oued Mechekel delivers however more clean waters (Figure 1). The surface area of the dam basin is 485 km^2, with a triangular compact shape (Belhadj et al 2011). The average annual temperature is 17 to 18°C, with annual rainfall of about 700 mm, which is relatively large, variable and irregular from one year to the next (Belhadj et al 2011). In summer, the two branches fall almost dry at the entering of Zit Amba reservoir, but its exit extruded low amounts to entertain some agricultural and stream environmental services. The water residence time (storage capacity/discharge (Ounissi & Bouchareb 2013) of the studied reservoir is largely variable according to the stream input, storage capacities and clogging rates. In 2012, the water residence reached 4 months. This is 7 folds lower than the residence time reported by Ounissi & Bouchareb (2013) in 2010.

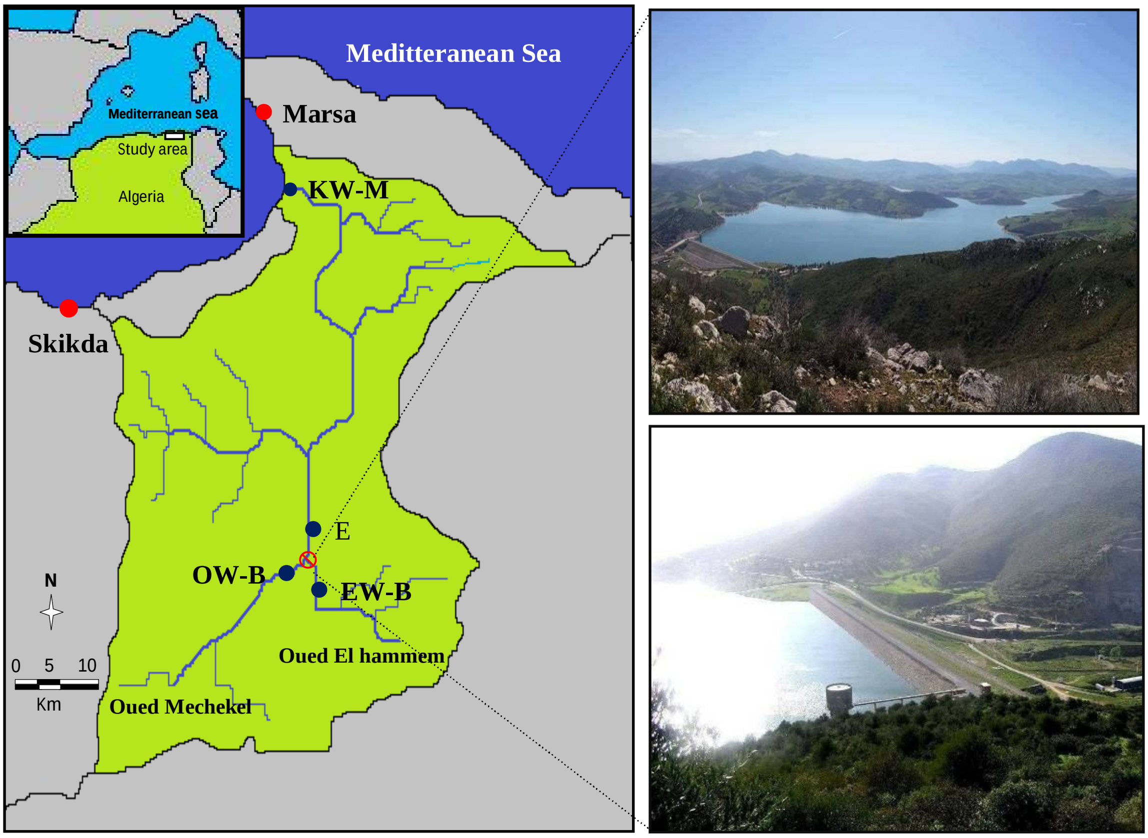

Figure 1. Study area and location of sampling stations. ⃠: Zit Amba reservoir; E-WB: entrance of Oued El Hammam branch; OW-B: entrance of Oued Mechekel branch; E: the exit and Zit Amba reservoir. KW-M: the mouth of Kebir West. On the right are views of Zit Amba dam.

Analytical methods. Jointly to water sampling, the flow velocity (m^3 s^{-1}) of the stream was assessed by the current meter CM-2 (Toho Dentan Co. Ltd, Tokyo). The flow (m^3 s^{-1}) was computed by multiplying the water velocity by the total surface area (m^2) of the streams' transect. The water flow, total suspended solids (TSS) and TDS were monthly measured during April 2012-March 2013 in 2 stations for Zit Amba reservoir (Figure 1) and 1 station for Kebir West catchment. Stations were located at the entrance and exit of Zit Amba dam and at the outlet of the Kebir West catchment (Figure 1). Measurements of water velocity were taken at several points depending on the station section size and depth. The TDS were measured (in milligram per liter or mg L^{-1}) in situ with the WTWi197 Multiparameter. In the laboratory the TSS were measured following the method described in Aminot & Chaussepied (1983). Two subsamples of 500 mL were filtered on pre-combusted (450°C for 1 h) and pre-weighed Whatman GF/C glass filters for TSS weight measurements. These filters were dried at 110°C for 1 hour by an oven dryer and then weighed with a Metler microbalance which provides a precision of 0.10 mg. For each filter, the TSS was obtained by subtracting the final filter weight (filter + TSS) from the initial weight of the filter, and the results were expressed in milligram per liter (mg L^{-1}). The instantaneous and annual TSS and TDS fluxes were assessed using the method of average instantaneous loads (Preston et al 1989).

Results

Water discharge into and from the Zit Amba dam and into the sea from the Kebir West outlet. The precipitation over Zit Amba sub-catchment reached 700 mm (Table 1). Water flow at the entrance of Zit Amba dam varied largely between 0.5-88.50 m^3 s^{-1} with an average of 12.1 m^3 s^{-1}, corresponding to 376.5 10^6 m^3 yr^{-1}. Zit Amba dam delivered between 0.3 and 14.6 m^3 s^{-1} and had an average of 7.8 m^3 s^{-1}, equivalent to 242.2 10^6

m^3 yr^{-1} (Table 1, Figure 2). Considering the received water discharge, Zit Amba reservoir seems to renewed every 4 month (residence time 4 month) (Table 1).

Table 1

Hydrological parameters of dam and river outlet studied during the study period (April 2012-March 2013)

			Catchment area (km²)	*Dam capacity (10^6 m^3)*	*flow (m^3s^{-1})*	*Volume* ($10^6 m^3$ yr^{-1})*	*Residence time (month)*	*Rainfall (mm)*
Dam sub-basin	Zit Amba dam	Entrance	450	120	12.1	376.5	4	700
		Exit	450	120	7.8	242.2	4	700
Lower KW catchement	KW outlet	outlet	1 450	-	12	386.1		742

* Volume of water received and delivered by the dam during the study period.

Water flow from the Kebir West outlet varied between 2 and 33 m^3 s^{-1} with an average of 12 m^3 s^{-1} (Figure 2) corresponding to an annual discharge of 386 10^6 m^3. During the dry period extending from May to August, the annual average of flow in the entrance in the entrance was 3.88 m^3 s^{-1} and 8.7 m^3 s^{-1} at exit due to the opening of the dam during this period. The outlet had received large freshwater amount during the wet season, reach 318.5 10^6 m^3.

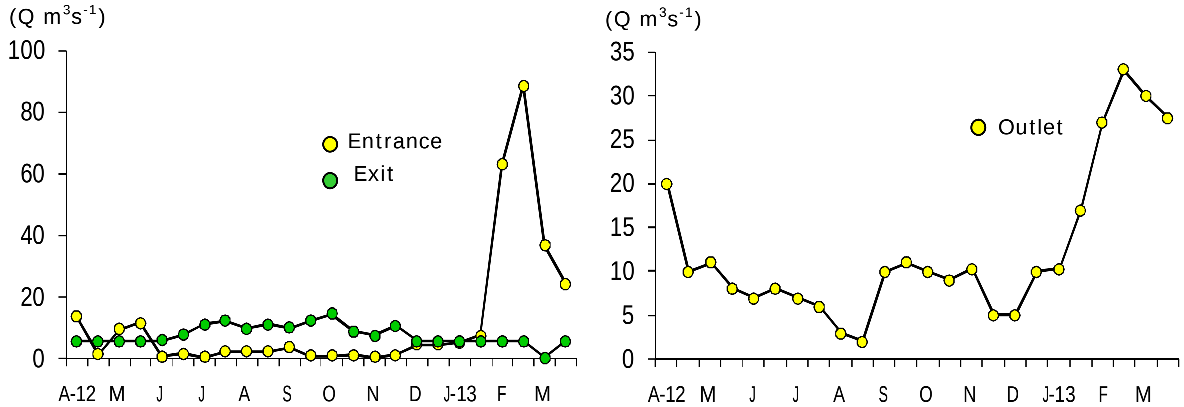

Figure 2. Water discharge (m^3 s^{-1}) at the dam entrance and exit of Zit Amba dam and at the Kebir West outlet during the Study period (April 2012-March 2013).

TSS and TDS level entrance and exit the dam and at the Kebir West outlet. The TSS levels of waters entering Zit Amba dam varied largely (4.3-66.3 mg L^{-1}) with an average of 16.7 mg L^{-1}. During the wet period TSS average amounts increased to reach 21.8 mg L^{-1} as can be seen in Figure 3. At the entrance of Zit Amba dam, the TDS levels ranged between 257.8-1.298 mg L^{-1} (Figure 3). In contrast to TSS seasonal cycle, TDS levels decreased to 547.9 mg L^{-1} during the wet period, but increased to 707.3 mg L^{-1} in the dry period. Water exiting Zit Amba dam were lowered by 35% in TSS levels and 30% in TDS levels, compared to the incoming amounts.

At Kebir West outlet the average annual level of TSS was 12.4 mg L^{-1}. The maximum value (15.7 mg L^{-1}) was recorded to the wet period and decreased to 5.87 mg L^{-1} in the dry period (Figure 3). This is because of sediment supply from agricultural lands, which spreads over the lower catchment, and is usually amended in winter, coinciding with the wet period.

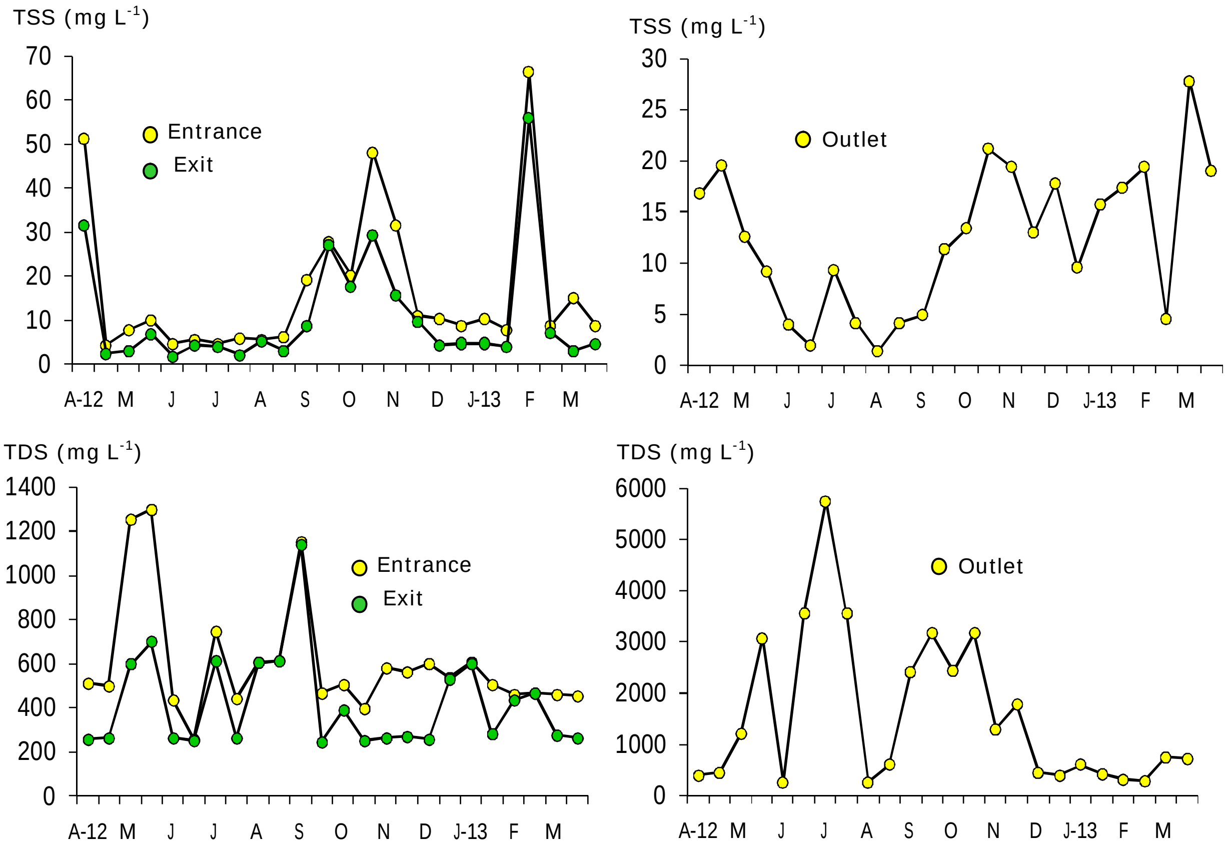

Figure 3. TSS and TDS levels (mg L^{-1}) at the dam entrance and exit and at the Kebir West outlet during the Study period (April 2012-March 2013).

TSS, TDS fluxes into and from the dam and at the Kebir West outlet. The delivered water into the Zit Amba dam brought annually 9 000 tons of suspended sediment, from which 67% (6 000 tons) is lost to the dam (Table 2). The erosion rate was 20 t km^2 yr^{-1} in sub catchment and 4 t km^2 yr^{-1} in the outlet during the study period. This difference is mainly due to the large amount of water discharge from the upstream of Zit Amba dam, and the exceptionally elevated rainfall height during the study period. The dam received annually 207 000 tons of dissolved solids, from which 49% (101 000 tons) is trapped (Table 2). The Kebir West outlet delivered annually to the sea 472 000 tons of TDS, and about half this amount resulted in dam release. The Zit Amba dam and the lower catchment have elevated soil degradation, as the specific salt losses reached in average about 325 to 460 t km^2 yr^{-1} (Table 2).

Table 2

Fluxes (t yr^{-1}) and specific fluxes (t km^2 yr^{-1}) of TSS and TDS from and into the dam and at the outlet during the study year (April 2012-March 2013)

		TSS *(10^3t yr^{-1})*	*TSS* *(t km^2yr^{-1})*	*TDS* *(10^3t yr^{-1})*	*TDS* *(t km yr^{-1})*	*TSS/TDS*
KW Dam	Entrance	9	20	207	460	4.34
	Exit	3		106		2.83
	R %	67		49		
KW River	Outlet	6	4	472	325	1.27

KW - Kebir West.

Discussion. The transfer of the dissolved and suspended solids across the aquatic continuum of the Kebir West catchment, from entrance the dam up to the catchment outlet was assessed in this study. The dam has received about 376.5 million m^3 of freshwater over the study year. The Kebir West outlet discharged into the sea 386.5 million m^3. The entrance of Zit Amba dam was heavily charged in TDS and weakly charged in TSS. As they were largely trapped in the dam, the sediment and salts amounts were remarkably reduced downstream the dams. The removal of sediment reached 67%, but retention of salts by Zit Amba was 49% (101 000) tons. In three dams (NE Algeria), Bouchareb (2013) reported more elevated sediment retention (70-92%) and salts retention (50-90%). Because of climatic and geologic factors, Algerian surface waters are known to be more salty than those of northern Mediterranean countries (Aubert 1976). Zit Amba dam trapped annually over 6 000 tons of TSS. Zit Amba dam seems thus to be affected by sediment deposition, and it is thus being submitted to severe and rapid clogging. Similar sedimentation was reported for Zerdaza dam, built on a contiguous Algerian catchment (Remini 2010; PNUE/PB 2003). The sediment loss reached a value as low as 20 t km^2 yr^{-1} for Zit Amba sub-basin. Sediment yields are highly variable in Algerian and Mediterranean coastal catchments and their dams (40-2780 t km^2 yr^{-1}) as shown in Table 3.

Table 3

Sediment loading (TSS, t km^2 yr^{-1}) for some Mediterranean and Algerian rivers and dams

River/dam opening	*t km^2 yr^{-1}*	*References*
Mediterranean rivers	251	UNEP/MAP/MED POL (2003)
Ebro River, Spain	214	UNEP/MAP/MED POL (2003)
Têt stream, France	40	Serrat et al (2001)
Rhône river, France	324	Pont et al (2002)
Italian rivers	780	UNEP/MAP/MED POL (2003)
Greece rivers	1140	UNEP/MAP/MED POL (2003)
Albanian rivers	2780	UNEP/MAP/MED POL (2003)
North African catchments	800	Fox et al (1997)
Maghreb catchments	397	Probst (1992)
Majrda, Tunisia	963	UNEP/MAP/MED POL (2003)
Moulouya, Morocco	250	UNEP/MAP/MED POL (2003)
Nile, Egypt	42	UNEP/MAP/MED POL (2003)
Cheliff, Algeria	78	UNEP/MAP/MED POL (2003)
Isser, Algeria	193	UNEP/MAP/MED POL (2003)
Kebir west, Algeria	200	UNEP/MAP/MED POL (2003)
Seybouse, Algeria	333	UNEP/MAP/MED POL (2003)
Soummam, Algeria	513	UNEP/MAP/MED POL (2003)
Tafna, Algeria	143	UNEP/MAP/MED POL (2003)
Cheffia dam, Algeria	2700	Touaibia (2010)
Charf dam, Algeria	300	Touaibia (2010)
Beni-Haroun dam, Algeria	64	Bouchareb (2013)
Zit El-Amba dam, Algeria	374	Bouchareb (2013)
Zerdaza dam, Algeria	192	Bouchareb (2013)
Chaffia dam, Algeria	143	Taamallah et al (2016)
Mexa dam, Algeria	371	Taamallah et al (2016)
Mafragh catchment’s outlet, Algeria	1974	Taamallah et al (2016)

Mean sediment yield of 61 t km^2 yr^{-1} has been reported by Meybeck & Moatar (2012) for 86 river catchments of semi-arid and temperate regions, which were daily surveyed for a long term. The Mediterranean river catchments (including Algerian coastal catchments) can be ranked among the most eroded areas, considering this world river catchment value. The sediment yield for Mediterranean rivers, as measured by UNEP/MAP/MED POL (2003) is around 580 t km^2 yr^{-1}, but because of the considerable reservoirs construction, the actual sediment flux is reduced to about 251 t km^2 yr^{-1}. In zit Amba dam the annual rétention of total dissolved solides (TDS) is about 100 000 tons. These values still however low compared to the world river mean (30 t km^2 yr^{-1}), noticed by Meybeck & Moatar (2012). Bouchareb (2013) reported low soil salt losses, ranging from 6-40 t km^2 yr^{-1}. When reaching the Kebir West outlet, soil loss increases to exceptionally high rate reaching 325 t km^2 yr^{-1}. This kind of soil degradation is 2.5 to 11-fold higher than that recorded in the Ebro River' outlet (Négrel et al 2007), for example. The net sediment flux that has attained the catchment outlet, issued from behind dam reached 6 000 tons.

Conclusions. This study highlights the following points:

- the water intercepted and stored in dam has led to a reduction in flow at the exit of dam by 36%;
- the delivered waters from the Zit Amba reservoir have high contents of total dissolved solids. Retention of TDS in the dam is in the order of 100 000 tons (50%);
- it is considered that the water of the basin studied, is on the other hand, and has a low content in TSS, particularly at the mouth of the river. The retention rate of TSS is 67% of the receiving sediment masses.

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ARTICLE 2: Water and nutrient transfers from a SW Mediterranean stream (Kebir West, Algeria) submitted to reservoir retention

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Water and nutrient transfers from a SW Mediterranean stream (Kebir West, Algeria) submitted to reservoir retention

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ABSTRACT

Kebir west catchment occupied 1,900 km^2 including Zit Amba reservoir that retain annually over 120 million m^3. The catchment is weakly populated with only 30 people/km², where the agricultural practices are still to subsistence need. Water samples were taken two times a month at the entrance and the exit of the reservoir, and the stream mouth during April 2012-April 2013 along. The aim of this study is to (a) the distribution of silicon (as well as nitrogen and phosphorus) in the catchment area under study, as a result of geochemical transfers at the river/sea interface, (b) to determine the effect of the dam on the retention of and nutrient salts and (c) to evaluate the fluxes of water and nutrient salts into the sea during the study period. The Kebir West reservoir delivered to the sea about 386 m^3/yr of water. From the inorganic nutrient incoming fluxes, the reservoir trapped annually 62% to 60% of DIN and DIP respectively and 56% of SiO_4. The mouth of the Kebir west stream delivered 274t/yr of total dissolved nitrogen in which the dissolved inorganic form represented 68%. Flux of total dissolved phosphorus reached 100t/yr with a great organic fraction (60%), while the amount of the dissolved silicon attained 923t/yr. Si:N molar ratio is still balanced (2.5-2.8) over the entire catchment, in contrast to N:P ratio deviated (9-11.40) from the Redfield standard ratio, indicating the prevalence of P over N. The dominance of P over N will have effects on the receiving coastal waters. The study concludes that the major characteristics of the water stream, under study, are marked by strong enrichment, in particular in NH_4 and PO_4, and retention of SiO_4 in the reservoir. The delivered waters from the reservoir have high contents of dissolved organic matter. This implies that these artificial impoundments would play a crucial role in nutrient biogeochemical cycling.

Key words: Kebir West, catchment, Stream, Reservoir, Flux, Nutrients, Algeria.

INTRODUCTION

During the recent decades water resources have been subject to various anthropogenic disturbances, including irrigation, dam retention and other needs of the population [32]. To meet the growing water needs, numerous dams have been built all around the Mediterranean Sea [13]. Mediterranean rivers flows are then experiencing large reduction by at least 20 % over the last 40 years [14]. Nutrient fluxes into and out of the sea water are strongly controlled by the associated water fluxes [31]. Also, for specific irrigation dams, river nutrient discharge decreases with the increasing rate of water and nutrient uptake by crops [34]. Dams may have a strong impact on the water and nutrient river discharge due to silicate (Si) and phosphorus (P) retention within sediments [1, 7]. Nitrogen, phosphorus and silicon are crucial elements for maintaining biological productivity in sea water. In the Mediterranean as a whole, concentrations and stocks of these elements are controlled by the

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exchange through the Straits of Gibraltar and the Bosphorus, by atmospheric deposition, by river and groundwater discharge and by anthropogenic point sources [31]. In Algeria the surface water yield is very limited, about only 12 km^3 of which 7 km^3 are retained in the dams [5]. In addition to the direct degradation, dam's construction, mainly used to irrigate about a million hectares of Algerian agricultural land [3], the cycle of the water basin scale is modified. In Algeria, investment infrastructure for water mobilization, supply and transfer currently represent 2% of the GDP. The construction of more than 30 dams over the past decade has increased the storage capacity of surface water to approximately 7 billion m^3 [4, 25]. Rivers play an important role in the global biogeochemical cycles by transferring dissolved and particulate substances from land to sea. By creating reservoirs in rivers, humans are substantially impacting the flux of sediments, organic matter and nutrients to the coastal zone [33]. The rivers play a particular role in supporting the Mediterranean production whose most productive zones are limited at the adjacent coast [8, 29]. Jointly to the reduction of the discharge and the silicon retained in large proportions in the dams, the fluxes in nitrogen (N) and in phosphorus have increased 3-5 times [17,14] and the Si/N/P ratios altered. Urban and agricultural nutrient inputs and water residence time within reservoirs also lead to change the nutrients Redfield ratios [14]. In addition, most studies about impacts of reservoir and river export of nutrients to the sea did not take into account organic compounds. However, some studies reveal that, even if the dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) are important components of riverine inputs and coastal catchments [22, 36], they are rarely considered within nutrient loadings pool. For example, Wiegner et al. [36] reported that DON often dominates the total dissolved nitrogen (TDN), but yet it is not considered to affect coastal water quality because it is assumed to be refractory. The authors add that DON needs to be considered into coastal nitrogen loading budgets, because of its rapid bioavailability as well as its atmospheric deposition in watersheds that forms about 15–30 % of the total bioavailable dissolved nitrogen [35]. In addition, data on river nutrient loading to the Mediterranean catchments are also scarce and are missing in the Southern Mediterranean countries [12, 14], despite that some data on dam retention of water and nutrients have been published [18, 2, 28]. The objective of this study it to estimate nutrient (N, P and Si) fluxes and dam effects on the biogeochemistry from the Kebir West catchment and the effects of reservoir on water and nutrient retention.

MATERIAL AND METHODS

Sampling site:

Kebir West catchment occupied an area of 1,900 km ^{2} (Fig. 1), but very weakly populated, with only 30 people/km^2 and it is managed by Zit Amba reservoir (120 million m^3 storage capacity). Zit Amba reservoir is used for irrigation and drinking water. The lower part of the catchment is affected by marine intrusion and functions in the dry period as a core estuarine area, which does not exceed several kilometers [18]. Zit Amba reservoir is fed by tow tributaries of Kebir West stream, with Oued El hammam at the south and at the west Oued El hammam. Oued El hammam is submitted to some urban pollution sources and hydrothermal used water, but Oued Mechekel delivers however more clean waters (Fig. 1). The sub-catchment of Oued El hammam is more forested and mainly occupied by olives trees and agricultural land. The lower area of Kebir West catchment is weakly populated, but being largely occupied by intensive agricultural activities. The catchment receives an annual precipitation yield varying generally between 800-900 mm [15]. During April-Mars 2012 the precipitation amount over the catchment was 730 mm. Titi Benrabah et al. reported a precipitation yield of 664 mm and 100.5 mm as height discharge (about 18 m^3 s^{-1}) for 2010. In summer, the two branches fall almost dry at the entering of Zit Amba reservoir, but its exit extruded low amounts to entertain some agricultural and stream environmental services. The water residence time (storage capacity/discharge [18] of the studied reservoir is largely variable according to the stream input, storage capacities and clogging rates. In 2012, the water residence reached 4 months, but was very weakly renewed during 2010 (28 months) [18].

Analytical methods:

Jointly to water sampling, the flow velocity (m s^{-1}) of the stream was assessed by the current meter CM-2 (Toho Dentan Co. Ltd, Tokyo). The flow (m^3 s^{-1}) was computed by multiplying the water velocity by the total surface area (m^2) of the streams' transects. Hydrological variables, nutrients and particulate matter were measured twice a month from April 2012 to April 2013 at five stations of Kebir West catchment. Sampling stations were located at the entrance and exit of reservoir and at the outlet of the respective stream. Kebir West stream was however sampled from the entrances of the West and Kebir branches (Fig. 1). 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 (0.5 mm porosity), dissolved inorganic nitrogen DIN (ammonia: NH_4; nitrate: NO_3; nitrite: NO_2), dissolved organic nitrogen (DON), phosphates PO_4 and silicates (SiO_4) were determined by means of standard colorimetric methods described in Parsons et al. Total dissolved phosphorus (TDP), polyphosphate (P_2O_5), and dissolved organic phosphorus DOP were measured following the standard method of Rodier. In this study, only the dissolved inorganic phosphorus (DIP) was considered as the sum of PO_4 and P_2O_5. The instantaneous fluxes of nutrients were calculated by multiplying their concentrations by the stream flow. The annual loads of nutrients were estimated using the method of average instantaneous loads [20]. Calculation of average loads of nutrients entrance to the Zit Amba reservoir was weighted for each tributary (Eastern and Western branches) by their respective water discharge. Nutrient retention in the Zit Amba reservoir represents the mean values of Western and Eastern branches compared to the exit reservoir one.

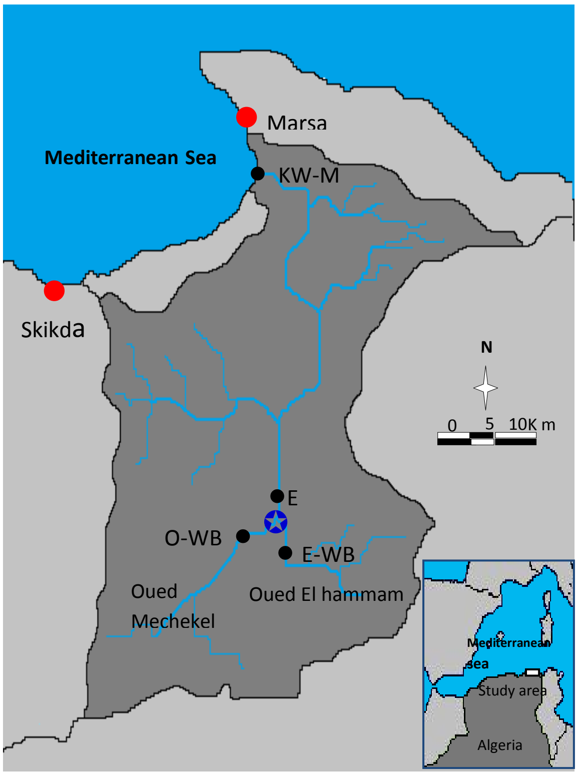

Fig. 1: Study area and location of sampling stations of the Kebir West catchment. ✪: Zit Amba reservoir; O-WB: entrance of Oued El-Hammam branch; O-WB: entrance of Oued Mechekel branch; E: the exit and Zit Amba reservoir. KW-M: the h of Kebir West outlet.

Results:

Nutrient concentrations and discharge at the entrance and exit of the reservoir:

The study period was an exceptional heavy rainfall so that the streams flow feeding Zit Amba reservoir has introduced strong water amount, where the discharge reached 12 m^3/s in average (Fig. 2i). The reservoir received during the year of April 2012 to March 2013 over 376 million m^3. At the exit the average of water discharge reach 7.61 m^3/s. During the study period, concentration of the total dissolved nitrogen (TDN) at the entrance of Zit Amba reservoir varied between 18 and 96 µmol/l (Fig. 2f) with an annual average of 43 µmol/l. The concentration of TDN decreased in the exit of the reservoir by only 9% (Tab 1) to reach 39 µmol/l. The maximal concentration of TDN found in a wet period with an average of 46 µmol/l in the entrance and in the exit 42 µmol/l. In fact, dissolved inorganic nitrogen (DIN) concentration at the exit decreased by 34% (Tab 1) compared to the entrance ones (Fig. 2d). The spatial and temporal fluctuations in concentration of dissolved organic nitrogen (DON) were relatively high varying between 5 and 25 µmol/l (Fig. 2e) at the entrance of the Zit Amba with an annual average of 11 µmol/ l. DON levels increased at the exit to 18 µmol/l (60%) (Tab 1), and the maximum concentration was found in the wet period (µmol/l). As can be shown (Fig. 2c) at the entrance of Zit Amba reservoir the nitrate (NO_3) concentrations varied from 1 to 57 µmol/l with an average annual value of 14µmol/l. At the exit of the Zit Amba the concentration of NO_3 decreased to reach an average annual of 10 µmol/l (retention of 25%) (Tab1), representing 27% of TDN. The NO_3 concentrations picked during the wet period. Zit Amba received large amounts of NH_4 (14.2 µmol/l), which represented 33.41%. However, the reservoir retained 38% of the incoming NH_4 amount. The reservoir acts here as a real remover that reduced the amount of DIN stock components (Tab 1). During the dry period, concentrations of NH_4 increased to 15 µmol/l at the entrance and 9 µmol/l at exit. In the wet period values were not so far from those of the dry period. At the entrance of the reservoir the seasonal evolution of NO_2 varied between 0.36-9 µmol/l (Fig. 2b) with an annual average of 3 µmol/ l only representing 7% of TDN. The concentrations of NO_2 at the exit were decreased by half the incoming stock (Tab 1).

Concentration of phosphate (PO_4) showed a clear spatial and temporal variability between 1 and 6 µmol µmol/l (Fig. 2g). The average annual was 3.45 µmol/ l at the entrance of the Zit Amba reservoir. At the exit the levels deceased to 2.27 µmol/l (34%; Tab. 1). The average concentration of total dissolved phosphorus (TDP) increased to 9.43 during the wet period at the opening of Zit Amba (Fig. 2j). The organic fraction (DOP) represented 53% of TDP. At the entrance of the Zit Amba reservoir, not only SiO_4 concentration was relatively elevated (81 µmol/l) but have experienced large reductions (29%; Tab.1) and was lowered to 57 µmol/l (Fig. 2k). Paradoxically, the concentration of SiO_4 during the wet period (86 µmol/l in average) was lower than the dry period (91 µmol/l). At the exit of the Zit Amba reservoir, SiO_4concentration followed remarkably those found at the entrance.

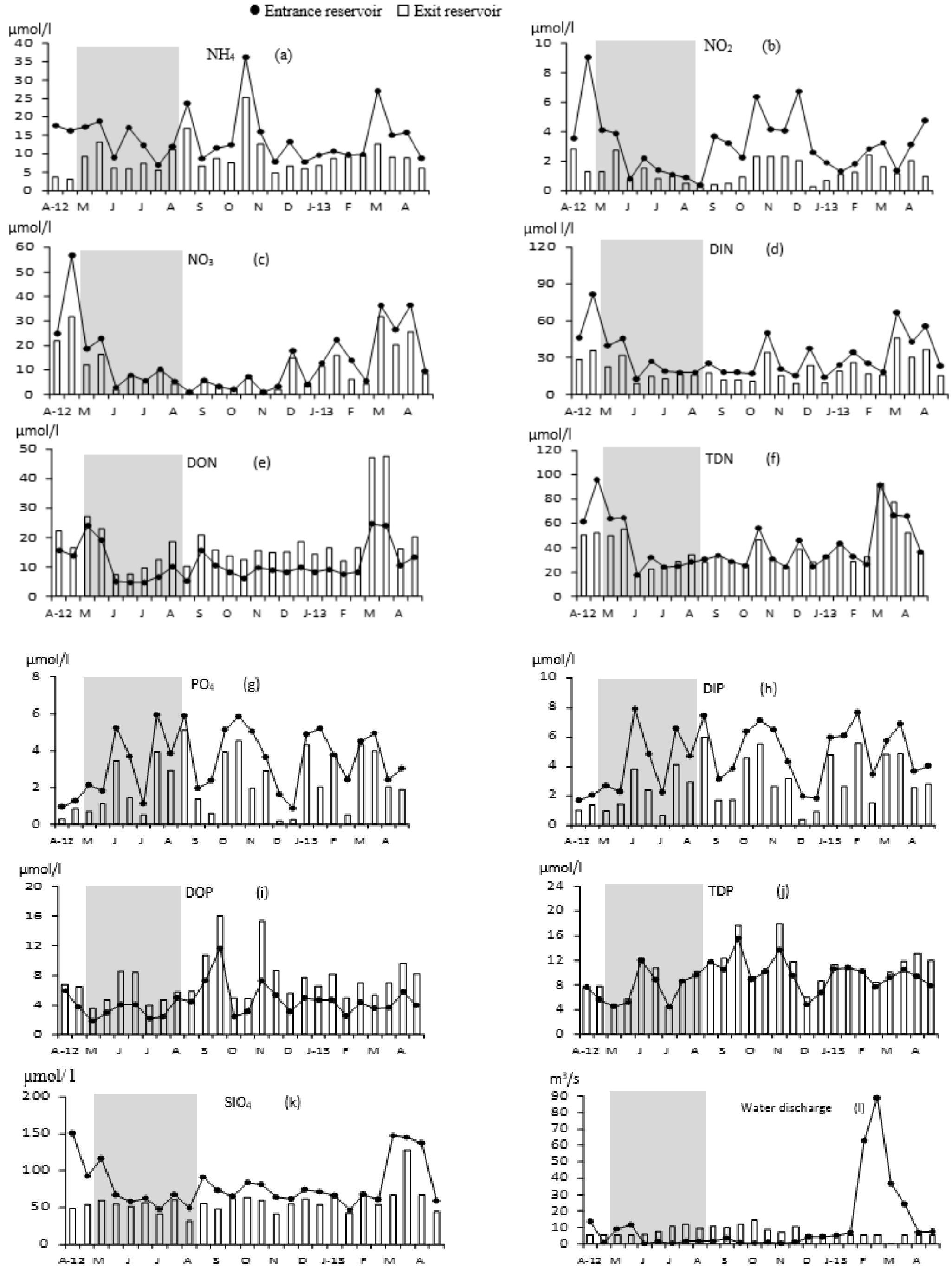

Fig. 2: Variations in nutrient concentration (µmol/l) and water discharge (m^3/s) at the entrance and exit of Zit Amba reservoir, April 2012- April 2013.

Table 1: Retention rates (%) at the Zit Amba reservoir. Negative values denote retention and positive ones denote release (April 2012-April 2013).

	NH_4	NO_3	NO_2	DIN	DON	TDN	PO_4	DIP	DOP	TDP	SiO_4
A1	-79	-11	-20	-38	+41	-18	-67	-41	+12	+1	-68
A2	-81	-44	-86	-56	+18	-45	-34	-32	+75	+37	-42
M1	-46	-35	-68	-43	+13	-22	-67	-64	+90	+11	-49
M2	-29	-28	-29	-29	+20	-14	-37	-37	+54	+9	-19
J1	-31	-29	-9	-29	+46	-8	-34	-52	+114	+4	-11
J2	-66	-6	-29	-45	+57	-30	-60	-51	+108	+22	-10
J1	-40	-13	-38	-32	+94	-6	-52	-71	+83	+5	-13
J2	-20	-6	-11	-11	+85	+15	-34	-38	+87	+0	-11
A1	-7	-23	-42	-13	+82	+21	-24	-38	+17	+6	-35
A2	-29	-32	-40	-29	+87	-8	-14	-19	+33	+0	-39
S1	-22	-12	-88	-33	+34	-2	-28	-46	+45	+18	-34
S2	-25	-9	-84	-33	+47	-3	-74	-55	+37	+14	-3
O1	-38	-10	-58	-37	+63	-4	-24	-29	+96	+7	-25
O2	-30	-12	-64	-32	+99	-17	-23	-23	+59	+2	-26
N1	-21	-55	-45	-27	+58	0	-61	-60	+112	+31	-35
N2	-38	-42	-43	-40	+66	-1	-20	-26	+64	+24	-11
D1	-50	-17	-70	-38	+82	-16	-86	-81	+83	+20	-16
D2	-23	-16	-89	-33	+87	+16	-68	-49	+56	+28	-26
J1-	-28	-10	-64	-21	+71	+3	-12	-19	+41	+7	-2
J2	-19	-28	-14	-24	+77	-3	-61	-57	+74	+0	-10
F1	-5	-55	-30	-34	+55	-13	-2	-28	+95	+3	-1
F2	-4	-26	-15	-12	+98	+22	-78	-57	+62	+9	-11
M1	-54	-13	-49	-31	+91	+2	-4	-16	+51	+10	-55
M2	-40	-24	-15	-29	+98	+17	-19	-30	+94	+13	-12
A1	-44	-30	-35	-34	+52	-20	-16	-31	+68	+39	-51
A2	-30	-13	-79	-33	+50	-3	-38	-29	+106	+50	-24

Nutrient distribution and discharge at the stream outlet:

At the Kebir West outlet the water discharge varied throughout the year between 2 and 33 m^3/s, with an average of 13.70 m^3/s. In the wet period the discharge increased to 17 m^3/s and decreased to only 6.5 m^3/s.

At the Kebir West outlet the average annual concentration in TDN was 46.31 µmol/l and the dominant form was DIN with annual average of 31.34 µmol/l and represented 68% of the TDN (fig. 3). In the wet period the average concentration in TDN was 48.28 µmol/l where 35% were in the form of dissolved organic form (DON). In the dry period the average concentration decreased to 42 µmol/l from which the inorganic form represented 73%. Within the inorganic nitrogen, NH_4 was important component in all periods, forming about third the dissolved nitrogenous stock (fig. 3).

The outlet of Kebir West had high concentrations of PO_4, with an average of 2.76 µmol/l according to the year. The concentrations of polyphosphate were low throughout the year with an average not exceeding 0.83 µmol/l (fig. 3). The average annual concentration in TDP was 9 µmol/l in which the organic form was dominant (60%) with an average of 5.35 µmol/l (fig. 3).The delivered waters into the neighboring coast were heavily loaded with TDP all over the year, but in the wet period the levels slightly increased to 9.14 µmol/l. Here the DIP constituted 40% the TDP. In the dry period the average concentration was 6.60 µmol/l, with the organic form represented 57 %.

The average annual concentration in SiO_4 was 78 µmol/l (fig. 3), and the high level was found in the wet period reaching 83 µmol/l and decreased to only 67.6 µmol/l in the dry period.

The delivered waters from the Kebir West outlet were highly disturbed as N:P molar ratio deviated from the Redfield ratios and reached 22.2. In contrast, Si:N was balanced (3.2) and TDN:TDP was about 7 and DON:DOP reached 18.

Nutrient fluxes into and from the reservoir and at the stream outlet:

The Zit Amba reservoir seems to act as nutrient trapper because it retained large masses of dissolved inorganic nutrients. It has removed 107, 528 and 20 t/yr of DIN, $S\text{-}SiO_4$ and $P\text{-}PO_4$, respectively. Fluxes of nutrients reaching the neighboring coast across the Kebir West outlet fluctuated in all season correlatively to the stream flow variability. Fluxes of all nutrients were largely enhanced by the strong rainfall (Tab 2) deploying the region in study period, which generated very high discharges to the sea. DIN load at the stream outlet was 186 t/y (Tab. 2) from which NO_3 contributed to 37%; DON 32% and NH_4 27% the total TDN load. These deliveries could be more elevated if the amounts removed by the dam can be considered. All DIN forms were largely trapped in the dam, particularly NO_3 (68 %), but the DON was slightly removed within the dam (14%).

At the opposite DON, Zit Amba reservoir produced some low amounts of DOP in the order 34%. Loads of DIP and TDP were 40 and 100 t/yr respectively. The fluxes of $Si\text{-}SiO_4$ delivered from Kebir West outlet were high reaching 923 t/yr. As shown in table 2, the Redfield loading have been modified due the dam retention, which can be considered as biogeochemical transformer, retaining inorganic nutrients and producing the dissolved organic form.

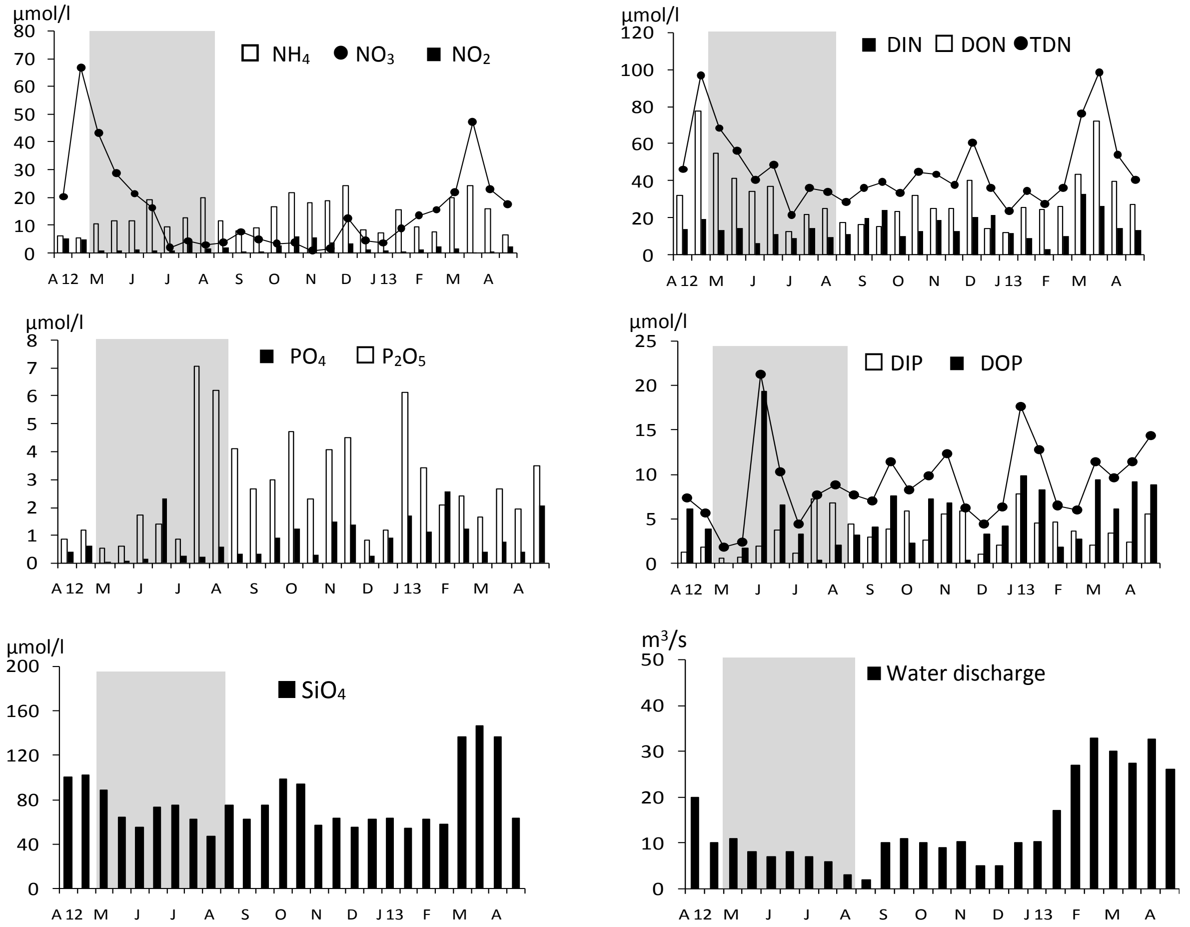

Fig. 3: Variations in nutrient concentration (µmol/l) and water discharge (m^3/s) at the mouth of Kebir West stream, April 2012- April 2013.

Table 2: Annual nutrient fluxes from and into the reservoir Zit Amba and at the respective stream outlet.

		KW reservoir						KW Stream
		Entrance	Exit	drinking water	Irrigation	Total out put	R/P %	Outlet
Volume	(106 m^3)	376	242	9	4	255		386
NH_4	(t/yr)	73	31	1,14	0.60	32,74	-55	73
NO_2	(t/yr)	14	4	0,17	0,08	4,25	-70	12
NO_3	(t/yr)	85	26	1,25	0,33	27,58	-68	101
DIN	(t/yr)	172	61	2,55	1,01	64,56	-62	186
DON	(t/yr)	69	56	2,29	0.89	59,18	-14	88
TDN	(t/yr)	241	117	4.85	1,22	123	-49	274
PO_4	(t/yr)	39	18	0,64	0,33	19	-51	30
TDP	(t/yr)	102	79	2,81	1.40	83	+19	100
DOP	(t/yr)	44	56	1,98	1	59	+34	60
DIP	(t/yr)	58	22	0,8	0.39	23	-60	40
SiO_4	(t/yr)	937	388	14,56	6	409	-56	923
N:P	(g/g)	13	21					22
Si:N	(g/g)	3,02	3,38					2,93

Discussion:

This work aimed mainly to estimate the transfer of N, P and Si in the Kebir West catchment to the inshore waters and to determine the dam effects on the biogeochemical transformations of these nutrients from behind the dam up to the stream outlet. From the entrance of dam until the stream outlet all nutrients displayed important biogeochemical transformations. In terms of concentrations, the inorganic nutrients were greatly trapped in Zit Amba reservoir: 34% for the DIN; 38% for DIP. By contrast, the organic nutrients were greatly produced at by the reservoir and delivered at its exit at 60% for DON and 65% for DOP. Under semi-arid Mediterranean climate in Australia, Cook, [6] reported that PO_4 have been retained at 77%; NO_3 (92%) and SiO_4 to 39% by the Lake reservoir, in term of the concentrations. In terms of loading the incoming fluxes of DIN and DIP were submitted to relative great retention compared to the SiO_4 which are retained at 62 and 60% respectively. These rates of retentions are small when compared to those of the same reservoir where the DIN was retained at 67% and DIP 83% [18]. In the temperate reservoir of Iron Gate I built on the Rhine River, Humborg et al. [11] reported that over 80% of dissolved Silica reduction can be related to the retention by the reservoir. Also in the temperate reservoirs of Marne, Seine, and Aube, Garnier et al. [9] reported relative low retention of $N–NO_3$ (40%) and more elevated rates for Si (50%) and (60%) for $P–PO_4$. These retention rates are just comparable to SiO_4 loads crossing the Zit Amba reservoir. This result shows an important production of the dissolved organic matter (DON) and (DOP) by Zit Amba reservoir, which trapped annually about 60% for DON and 65% for DOP entering the reservoir.

The Kebir West catchment had high DOP values compared to those recorded in continental waters that usually fluctuated around 0.5 µmol/l. However, Prasad and Ramanathan [21] recorded comparable values reaching in average 6 µmol/l in a mangrove estuarine system under summer conditions. The DON values in Kebir West catchment from 3 to 33 µmol/l. In Northern Italia, Arno and Po have strong DON content with 135 and 142 µmol/l. In Ebro and Rhone, organic nitrogen concentrations were 34 and 25 µmol/l [31]. Globally, the high dissolved organic matter values coincided with low discharges and, on the contrary, the low values rise with high water flow. Therefore, a fraction of the retained inorganic nutrients would have served to produce DON and DOP in the Zit Amba reservoir. In term of specific fluxes the DIN delivered to the sea is 98 $kg/km^2/yr$ and also important masses of $P-PO_4$ (16 $Kg/Km^2/yr$), the DIN specific loadings from the Seybouse outlet were high, ranging from 77 to 640 kg/ km^2/yr, depending on the year and 2 to 15 $kg/km^2/yr$ for $P-PO_4$ [18, 2]. $N-NO_3$ delivered to the sea is 53 $kg/km^2/yr$ compared to fluxes are measured on the South Mediterranean Rivers, Southern Spain, South and Western Turkey with, for most rivers, less than 100 $kg/km^2/yr$ [31]. Most of large Mediterranean rivers [14, 17, 31] have specific fluxes superior to the values of the present study.

On the other hand, DON was often omitted in nitrogen pool budget and cycling, but this study show that significant amounts of DON (46 kg/ km^2/yr) can be introduced to the sea, . In comparison, the amount of the DON that was introduced to coastal water by Seybouse River is 6 to 58 $kg/km^2/yr$ depending on the year [2]. This suggests that DON which even can contribute appreciably to the marine eutrophication, should be considered [27] in monitoring programs.

The delivered waters from the reservoir were highly disturbed in term of Redfield ratios. The other negative role of reservoirs would be the modification of the loading Redfield ratios, changing from relative balanced values to high and altered ones. The loading ratios of N:P was 9 entrance and increased to 17 exit. The loading ratios Si:N still however unchanged along with the aquatic continuum of the catchment. The intensification of the agricultural practices and the recent reduction of the phosphates in the laundries contributed to increase the N:P ratio considerably. Therefore, the production of the inshore marine phytoplankton would be controlled mainly by phosphorus. Nevertheless, the Si/N ratio in the Kebir catchment was always >1 and can support the requirements of diatoms [24] in contrast to the major world rivers which experience a large decrease of the Si/N ration and can encompass the marine ecosystem functioning [5, 23,11].

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 that was retained in the reservoir. Overall, the water and nutrient transfer in the stream-reservoir system can be summarized as follows:

- It is considered that the water of the basin studied, is on the other hand, and has a low content in SiO_4, particularly at the mouth of the river.
- The river flows into the Zit Amba dam are particularly heavily polluted by NH_4 and PO_4.
- All the dissolved mineral nutrients undergo considerable retention in the dam, constantly exceeding 50% of the fluxes at entrance.
- Inorganic nitrogen and phosphorus are particularly retained at rates of up to 62% for N and 60% for P.
- Due to nutrient entrapment in the dam, the fluxes to the sea are significantly reduced.
- The water intercepted and stored in dam has led to a reduction in flow at the exit of dam by 34%.
- The delivered waters from the Zit Amba reservoir have high contents of dissolved organic matter, which implies that the retained matter would play a crucial role in nutrient biogeochemical cycling. Such changes would have considerable impact on the hydrological and biogeochemical properties of the river systems and on the functioning and the productivity of the receiving coastal waters.

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FIGURES CAPTION LIST

TABLES CAPTION LIST

List of abbreviations

NH_4: Ammonia nitrogen (NH_4^+ + NH_3) also noted NH_4^+
NO_3: Nitrate ion also noted NO_3^-
NO_2^-: Nitrite ion also noted NO_2^-
DIN: Dissolved inorganic nitrogen
DON: Dissolved organic nitrogen
PO_4: Phosphate ion also noted PO_4^{-3}
$Si(OH)_4$: Silicic acid also noted SiO_4
N: Nitrogen
P: Phosphorus
Si: Silicon
BSi : Biogenic silica
POC : Particulate organic carbon
POC1: the fraction of particulate organic carbon <200 µm ≈phytoplakton
POC2: the fraction of particulate organic carbon >200 µm ≈zooplakton
TSS: Total suspended solids (mg L^{-1} or mg /L)
TDS: Total Dissolved Solids or freshwater salinity (mg L^{-1} or mg /L)
EC: Electrical conductivity (micro-simens or µS/cm)
Mg L^{-1}: Milligram per liter
KR: Kebir-Rhumel stream
R-DO: Rhumel Branch (entrance Beni-Haroun dam)
K-DO: Kebir Branch (entrance Beni-Haroun dam)
KR-DE: Exit Beni-Haroun dam
KR-M: Kebir-Rhumel stream's mouth
KR-DO: Kebir -Rhumel dam entrance
KW: Kebir west stream
OW-B: Oued el mechekel the entrance of Zit Amba
EW-B: Oued el hammem the entrance of Zit Amba
EW-B: exit dam Zit-Amba
KW-DO: Kebir West dam entrance
KW-DE: Kebir West dam exit
KW-M: Kebir West stream's mouth
SF: Saf-Saf stream
SF-DO: Entrance Zerdaza dam
SF-DE: exit Zerdaza dam
SF-M: Saf-Saf stream's mouth
N:P:N standard Redfield ratios of the atomic composition of the water and aquatic organisms
ABH: Hydraulic Basin Agency
ANRH: National Agency for Water Resources
ONIT: National Office of Irrigation and Transfer
ONA: National Office of Sanitation
ADE: Water Distribution Agency
ANB: National Agency for Dams
PIB: Gross National Product
ONED: National Observatory for the Environment and Sustainable Development
ANBT: National Agency for Dams and Transfer