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Nutrient distribution in the Bay of Annaba under the influence of the Seybouse and the Mafragh estuaries inputs (South-Western Mediterranean)

Par

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To my mother, my father,
my sister and brothers
my wife and children
for their support and encouragement throughout the long years.

Foreword

The writing of a thesis is often a long and arduous experience, especially in the English language which gives to work more and more to cover the linguistic difficulties that the one feels; but rewarding in many points of view because it allows in particular to remember the many difficulties of field, meetings and collaborations that have enabled its completion.

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Abstract

Dissolved inorganic nitrogen (DIN), phosphate (PO_4) and silicic acid ($Si(OH)_4$) loads from the Seybouse and the Mafragh estuaries and from wet atmospheric deposition into the Bay of Annaba, were assessed at three stations of the Bay over three years. The Seybouse inputs had high levels of DIN and PO_4, in contrast to the Mafragh estuary's near-pristine inputs; $Si(OH)_4$ levels were low in both estuaries. The N:P molar ratios were over 30 in most samples and the Si:N ratio was less than 0.5 in the Seybouse waters, but nearly balanced in the Mafragh. The specific fluxes of Si–$Si(OH)_4$ (400–540 kg Si km^{-2} yr^{-1}) were comparable in the two catchments, but those of DIN were several-fold higher in the Seybouse (373 kg N km^{-2} yr^{-1}). The inner Bay affected by the Seybouse inputs had high levels of all nutrients, while the Mafragh plume and the outer marine station were less enriched. In contrast to the most Mediterranean regions, the Bay of Annaba received low nutrient masses from wet atmospheric inputs, which did not exceed 2-3 % of the total loads. The atmosphere was found to be a weak source of nutrients, when compared to the Seybouse and Mafragh estuaries contribution. The nutrient wet atmospheric molar ratios were found disturbed (N:P = 28 and and Si:N = 0.34) as for the Seybouse waters.

Key-words:
Nutrients, Flux, Estuary, Coastal water, Atmospheric deposition, Annaba Bay

Résumé

Les flux de l'azote inorganique dissous (NID), phosphate (PO_4) et de l'acide silicique ($Si(OH)_4$) des estuaire Seybouse et Mafragh et des dépôts atmosphériques humides dans la baie d'Annaba, Algérie, ont été évalués à trois stations de la baie pendant trois ans. Les décharges de Seybouse étaient élevées surtout pour NID et PO_4 contrairement aux eaux propre de l'estuaire Mafragh; les flux de $Si(OH)_4$ étaient faibles dans les deux estuaires. Les rapports molaires DIN:PO_4 étaient plus de 30 dans la plupart des échantillons et le rapport $Si(OH)_4$:DIN est inférieur à 0,5 dans les eaux Seybouse, mais proche de l'équilibre dans la Mafragh. Les flux spécifiques de Si-$Si(OH)_4$ (400-540 kg Si km^{-2} an^{-1}) étaient comparables dans les deux bassins versants, mais ceux de NID étaient plusieurs fois plus élevée dans la Seybouse (373 kg N km^{-2} an^{-1}). L'intérieur de la baie affectée par les décharges de Seybouse présente des quantités élevées de tous les nutriments, tandis que le panache Mafragh et de la station maritime extérieur étaient moins enrichis. La baie de Annaba recevait une contribution de 3, 2 et 2% pour le NID, PO_4 et SiO_4 respectivement par rapport aux apports totaux. Les rapports molaires atmosphériques ont été trouvés à 28 et 0,34 pour DIN:PO4 et SiO4:DIN respectivement. L'atmosphère s'est révélée être une faible source de nutriments dans les eaux de surface de la baie de Annaba par rapport aux flux de Seybouse et Mafragh, ces sources continentales qui doivent être préservés.

Mots-clés :
Nutriments, Flux, estuaire, eaux côtières, les dépôts atmosphériques, baie de Annaba

ملخص

تدفق النيتروجين غير العضوي المذاب (DIN) الفوسفات (PO_4) و حمض السيليسيك ($Si(OH)_4$) من مصبات الأنهار سيبوس و مفرغ و كذلك الترسبات الجوية الرطبة في خليج عنابة ، الجزائر، تم قياسها في ثلاث محطات في الخليج لمدة ثلاث سنوات. تصريفات سيبوس كانت عالية خاصة NID و PO_4 على عكس المياه النظيفة لمفرغ، تدفقات ($Si(OH)_4$) كانت ضعيفة في كل من مصبات الأنهار، النسب المولية $DIN:PO_4$ كانت اكثر من 30 في أغلبية العينات و النسبة $DIN:(Si(OH)_4)$ في مفرغ . التدفق النوعي $Si\text{-}Si(OH)_4$ (400 500 كغ Si/سنة) كانت متماثلة في كل من مستجمعات المياه و لكن NID كان عدة مرات اكثر في سيبوس (373 كغ . N. كم/سنة). الخليج الداخلي يتاثر بتصريفات سيبوس و لديه كميات عالية لجميع العناصر الغذائية في حين كانت محطة مفرغ و المحطة البحرية الخارجية أقل تخصيبا . خليج عنابة يستقبل مساهمة 3،2 و 2 % لـ NID، PO_4، SiO_4 على التوالي بالمقارنة مع مجموع المساهمات . النسب المولية الجوية كانت 28، 0.34، لـ PO_4:NID و $DIN:SiO_4$ على التوالي . المساهمة الجوية بالمواد المغذية في المياه السطحية لخليج عنابة مقارنة بتدفقات سيبوس و مفرغ، هذه المصادر للمياه الداخلية التي يجب المحافظة عليها .

الكلمات المفتتاحية:

المواد المغذية، تدفق، مصبات الانهار، المياه، الساحلية، خليج عنابة.

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General introduction

General introduction

Coastal zones with their resources are important for the development of human activities and are major contributors to economic prosperity, social well-being 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). Therefore their preservation becomes a first order priority for a stable socio-economic development in the Mediterranean region. Because of dense human populations in watersheds along the coastal zone; coastal waters are very sensitive to anthropogenic impacts (Cloern, 2001; Giordani et al., 2008; Howarth et al., 1996; Nixon, 2005). They are extremely variable systems, where fluctuations of land influences (Rivers, sewage flows) induce high temporal variability on scales ranging from hours to seasons (Walsh, 1988).

As Rivers provide the major source of nitrogen (N), silica (Si), and phosphorus (P) to coastal area and are coupled to their watersheds, fresh water management should be linked to coastal management (Nixon, 2005). In fact, as reported by Montagna et al. (2002), nothing is more fundamental to the functioning of a coastal area than the quantity and timing of freshwater delivery. In oligotrophic seas as the Mediterranean Sea, River inputs of nutrients do play a particular role in sustaining the marine productivity and zones of high productivity are therefore mainly limited to the coastal waters that receive major freshwater inputs (Bosc et al., 2004).

However, changes in the amount and ratios in riverine N, P and Si inputs to coastal ecosystems contribute to numerous negative human health and environmental impacts, such as loss of habitat and biodiversity, increase in blooms of some harmful algae species, eutrophication, hypoxia and fish kills (Billen and Garnier, 2007; Cloern, 2001; Diaz et al., 2008; Howarth et al., 1996; Turner et al., 2003). Also, the inorganic N and P fluxes to seas have already increased by at least a factor of three at a global scale (Bennett et al., 2001; Meybeck, 2003). For the Mediterranean sea Rivers, Ludwig et al. (2009) reported that fluxes of N and P were strongly enhanced by anthropogenic sources and their total inputs to the Mediterranean Sea could have increased by a factor >5. While a decrease can also be expected for the fluxes of dissolved silica (Si) which is strongly controlled by water discharge and potentially reduced by River damming as well. In addition, the gradual change in the Si:N Redfield ratio is responsible for the severe modification of coastal zone food-webs, including impacts on regional halieutic resources (Rabalais et al., 2009; Turner et al., 2003). Anthropogenic eutrophication in coastal environment results from increased delivery of land-based nutrients considerably enriched in N and P compared to Si (Brion et al., 2008; Ragueneau et al., 2006). When also considering Si as a limiting element, which is the case for siliceous phytoplanktonic species (diatoms), Humborg et al. (2000) reported that Si limitation may expand in the Mediterranean Rivers since the early decades and dissolved Si concentrations were reduced to less than half their pre-dam construction values in the Danube and Nile River. Construction of dams and other water structures to serve human needs will have an adverse impact on the diversity and productivity of coastal marine waters (Nixon et al., 2004; Conley et al., 2000). Humborg et al. (1997) observed a direct link between dam building, nutrient ratio, and coastal ecosystem structure in the Danube–Black Sea system. They also concluded that a dramatic change in nutrient loads and composition (Si:N:P ratios) entering coastal seas will have far reaching effects on coastal ecosystems. In the same context Turner et al. (1998) described how freshwater and marine ecosystems can undergo fundamental aquatic food web changes as diatom growth is compromised when the Si:DIN ratio falls below 1:1.

Therefore, a key topic of coastal research now centers around changes in the ratios and loading of N, P, and Si and the impacts of changing nutrient ratios on phytoplankton composition (Béthoux et al., 2002; Howarth and Marino, 2006). However, the study of River syndromes at a global or regional scale is still limited by the available information (Meybeck, 2003) and impacts of some River syndromes on aquatic resources are already considered as a first priority. The 1990s saw the launch of several global-scale programmes focusing on the coastal ocean and its connected River inputs: IGBP-LOICZ (http://www.loicz.org), GIWA (http://www.giwa.net/; GIWA, 2001) and the Large Marine Ecosystems (LMEs, http://www.edc.uri.edu/lme) as reported in numerous works Giordani et al., 2005, 2008; Meybeck et al., 2007; Viaroli et al., 2001, 2004. In the last decade, new GIS tools have been developed to characterize River catchments at the global-scale (Meybeck et al., 2006; Seitzinger et al., 2005; Vörösmarty and Meybeck, 2004).

Data on River nutrient loading to the Mediterranean basin is also scarce and are missing in many eastern and North African countries which bias the general picture (Ibáñez et al., 2008; Ludwig et al., 2009; Milliman, 2007). In Algeria, despite the strong lack of data on nutrient loads from River watersheds to the receiving shelf, no study has been performed until now on the distribution of dissolved nutrients in coastal areas in relation to River inputs. For the Bay of Annaba, the few published data are very limited in time and space scales and concerned only the distribution of the inorganic nitrogen and phosphate in the inner sector of the Bay of Annaba (Fréhi et al., 2007; Ounissi and Fréhi, 1999) and seasonal fluxes of the same nutrients from the Mafragh estuary (Khélifi-Touhami et al., 2006). The Bay of Annaba receives diffusive inputs from the Seybouse and the Mafragh estuaries in addition to direct urban and industrial wastes. The estuaries watersheds of about 10,000 km² inhabit together over two Million people where intensive agricultural practices have become the most important activities of the population in the last decade. The population increases and its activities suppose besides household wastes increase, a large amount of water retention in dams (Ounissi and Bouchareb, 2013) for irrigation needs and fertilizers uses that can induce changes in the adjacent coastal ecosystem functioning. The Seybouse estuary constitutes the major contributor. The industrial wastes of a big fertiliser factory delivered over 1 Million m^3d^{-1} of water heavily charged in ammonia and phosphate (Ounissi et al., 2008). Moreover, the direct and untreated domestic wastes delivered about 0.3 Million m^3 strongly loaded in ammonia and phosphate. Human influences and irregular hydrological regime are then the common features in Mediterranean River systems that affect both coastal and inland water characteristics.

The Mediterranean Sea is one of the most oligotrophic seas in the world (Krom et al., 2004; Pitta et al., 2005). Most of the nutrient inputs to the Mediterranean Sea are mainly originated from the atmosphere (including dry and wet depositions) and riverine runoff. Over the last four decades, the freshwater discharge from Rivers to the Mediterranean has suffered a substantial decrease owning to both climate change and dam constructions (Ludwig et al., 2009) therefore the relative importance of atmospheric inputs of nutrients to the Mediterranean surface waters will have increased.

There are two main sources that strongly affect the composition of atmospheric particles and precipitation in the Mediterranean area. One of these is the eolian dust transported from North Africa (Guerzoni et al., 1999; Kubilay and Saydam, 1995) and the other one is the pollution aerosol transported from Europe (Dulac et al., 1987; Bergametti et al., 1989; Gullu et al., 1998).

The Mediterranean has one of the highest fluxes of airborne mineral dust owning to its close proximity to arid regions, in particular the Saharan, Middle Eastern and Arabian Deserts (Loÿe-Pilot et al., 1986; Guerzoni et al., 1999; Kubilay et al., 1995, 2000; Koçak et al., 2004). Atmospheric deposition of desert dusts over the Mediterranean supplies soluble or bioavailable N, P and Si which influence ocean biogeochemistry (Herut et al., 1999, 2002, 2005; Guieu et al., 2002; Ridame and Guieu, 2002; Markaki et al., 2003, 2010; Bonnet et al., 2005; Carbo et al., 2005).

Atmospheric inputs of nutrients to the coastal system and the open ocean can take place through dry and wet deposition. According to Guerzoni et al. (1999), the atmospheric input of inorganic nitrogen represents 60% of the total nitrogen entering the Mediterranean from continental origin, 66% of which is via wet deposition. Unlike N compounds which have dominant anthropogenic sources (Spokes and Jickells, 2005) the aerosol P content and Si are of continental/natural origin (rock and soil) (Herut et al., 1999; Markaki et al., 2003; Baker et al., 2007).

Despite the direct anthropogenic influence on River flow, large-scale processes (meteorological pattern, weather patterns, large scale indices) impact the variability of the riverine nutrient discharges and that of the nutrients in the Bay. The north Atlantic oscillation (NAO), with centers of action near Iceland and the Azores, has long been identified as an influencing factor on Mediterranean climate variability, especially during winter (Ulbrich et al., 2012). The positive winter NAO is related to below-average precipitation rates over large parts of the western and northern Mediterranean region, with opposite deviations for the negative winter NAO (Trigo et al., 2004, 2006). The Mediterranean atmospheric winter water deficit is positively correlated with the NAO and has been increasing due to the long-term positive anomalies of the NAO since the early 1970s (Mariotti et al. 2002). Links of Mediterranean climate variability to tropical circulation anomalies have been identified. The most important one is the relation to the El Niño Southern Oscillation (ENSO), whose signals from the tropical Pacific area can be propagated downstream as a Rossby-wave train (Alpert et al., 2006), thus affecting regions like the Mediterranean region, far away from the Pacific origin of the dynamical signal. Correlations between ENSO and western Mediterranean rainfall have been found for spring and autumn, but with opposite signs: spring rainfall following ENSO warm events is decreased (Mariotti et al., 2002), whereas autumn rainfall preceding the mature warm phase of ENSO is increased (Mariotti et al., 2005). Over the 50-yr period the Mediterranean atmospheric water deficit increased by about 24% in the winter season, and by 9% annually (Mariotti et al., 2002). In contiguous Algerian catchments (Northeastern Algeria), Meddi et al. (2010) reported a decrease of at least 20 % of total annual rainfall from the mid-1970s. River discharges with their loads of nutrients into Mediterranean Sea is then doubly affected by the climatic variability and by dams retention. These factors can modulate the eutrophication impact upon these sensitive coastal systems.

The objectives of the present study were (1) to estimate nutrients (N, P and Si) fluxes from diffuse sources (Seybouse and Mafragh estuaries) and from atmospheric deposition; and (2) to assess how much that transfer influenced the temporal and spatial distribution of nutrient levels and ratios in the Bay of Annaba.

This study is a part of the environmental monitoring program involving the transfer of materials from the Seybouse and Mafragh basins to the coast (research projects: F3101/04/05 MESRS; F01120070008 MESRS; South European Seas Assessment and Modelling Ecosystem Exchange 2006/2009). It focuses on the hydrology and the importance of estuaries inputs in the functioning of the land-sea system interaction and their repercussion on the functioning and the productivity of the receiving coast, in particular nutrient loadings into the Bay of Annaba.

This manuscript is structured in four chapters; the first one is strictly documentary which provide a synthesis on the coastal environment features emphasising on the main features of the Mediteranean Sea, the estuaries, the Rivers water and the biogeochemistry of the nutrients (N, P, Si), objects of study in estuarine and coastal environments. The second chapter describes the study sites and sampling methods and chemical analyses. The third chapter presents the results of the hydrology and nutrient loads from the estuaries and the wet atmospheric deposition. The last chapter analyse the distribution of nutrients in the Bay of Annaba. The manuscript ended with a discussion of the results and give the main conclusions.

References

Alpert, P., Baldi, M., Ilani, R., Krichak, S., Price, C., Rodó, X., et al., 2006. Relations between climate variability in the Mediterranean region and the Tropics: ENSO, South Asian and African monsoons, Hurricanes and Saharan Dust. In: Lionello, P. Malanotte-Rizzoli., P. Boscolo, R. (Eds.), the Mediterranean climate: An overview of the main characteristics and issues. Elsevier, Amsterdam, pp. 149–177.

Baker, A.R., Weston, K., Kelly, S.D., Voss, M., Streu, P., Cape, J.N., 2007. Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: Links to primary productivity and nitrogen fixation, Deep-Sea Res. Part. II, 54: 1704–1720.

Bennett, E.M., Carpenter, S.R., Caraco, N.F., 2001. Human impact on erodible phosphorus and eutrophication: a global perspective. Bioscience 51 : 227-234.

Bergametti, G., Dutot, A.L., Buat-Menard, P., Losno, R., Remoudaki, E., 1989. Seasonal variability of the elemental composition of atmospheric aerosol particles over the north-western Mediterranean. Tellus, 41B: 353-361.

Béthoux, J.P., Morin, P., Ruiz-Pino, D.P., 2002. Temporal trends in nutrient ratios: chemical evidence of Mediterranean ecosystem changes driven by human activity. Deep-Sea Res. Part II 49 (11): 2007–2016.

Bonnet, S., Guieu, C., Chiaverini, J., Ras, J., and Stock, A, 2005. Effect of atmospheric nutrients on the autotrophic communities in a low nutrient, low chlorophyll system, Limnol. Oceanorg., 50(6): 1810–1819.

Billen, G., Garnier, J., 2007. River basin nutrient delivery to the coastal sea: assessing its potential to sustain new production of non siliceous algae. Mar. Chem. 106: 148-160.

Bosc, E., Bricaud, A., Antoine, D., 2004. Seasonal and inter-annual variability in algal biomass and primary production in the Mediterranean Sea, as derived from 4 years of Sea WiFS observations. Global Biogeochem. Cy. 18. DOI:10.1029/2003GB002034.

Brion, N., Andersson, M.G.I., Elskens, M., Diaconu, C., Baeyens, W., Dehairs F., Middelburg, J,. 2008. Nitrogen cycling, retention and export in an eutrophic temperate macrotidal estuary. Mar. Ecol. Progr. Ser. 357: 87-99.

Carbo, P., Krom, M. D., Homoky,W. B., Benning, L. G., and Herut, B. 2005. Impact of atmospheric deposition on N and P geochemistry in the southeastern Levantine basin, Deep-Sea Res. Pt. II, 52: 3041–3053,.

Cloern, J., 2001. Our evolving conceptual model of the coastal eutrophication problem. Mar. Ecol. Progr. Ser. 210: 223-253.

Conley, D.J., Stalnacke, P., Pitkanen, H., Wilander, A., 2000. The transport and retention of dissolved silicate by Rivers in Sweden and Finland. Limnol. Oceanogr. 45 (8): 850–853.

Diaz, F., Naudin, J.J., Courties, C., Rimmelin, P., Oriol, L., 2008. Biogeochemical and ecological functioning of the low-salinity water lenses in the region of the Rhone River freshwater influence, NW Mediterranean Sea. Cont. Shelf Res. 28: 1511-1526.

Dulac, F., Buart-Menard, P., Arnold, M., Ezat, U., Martin D., 1987. Atmospheric input of trace metals to the Western Mediterranean sea: 1. Factors controlling the variability of atmospheric concentrations. J. Geophys. Res., 92: 8437-8453.

Fréhi, H., Couté, A., Mascarell, G., Perrette-Gallet, C., Ayada, M., Kara, M.H., 2007. Dinoflagellés toxiques et/ou responsables de blooms dans la baie d'Annaba (Algérie). C. R. Biol., 3(30) : 615-628.

Giordani, G., Austoni, M., Zaldívar, J.M., Swaney, D.P., Viaroli, P., 2008. Modelling ecosystem functions and properties at different time and spatial scales in shallow coastal lagoons: An application of the LOICZ biogeochemical model. Estuar. Coast. Shelf S. 77: 264-277.

Giordani, G., Viaroli, P., Swaney, D.P., Murray, C.N., Zaldívar, J.M., Marshall Crossland, J.I., 2005. Nutrient fluxes in transitional zones of the Italian coast. In: LOICZ Reports & Studies, No. 28. LOICZ, Texel, the Netherlands, pp. ii+157.

GIWA Core Team, 2001. GIWA Methodology, Stage 1: Scaling and Scoping, Guidance to the Methodology and its Use. Global Intl. Waters Assess, Kalmar, Sweden. 104 pp.

Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loÿe-Pilot, M. D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., and Ziveri, P., 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean sea, Prog. Oceanogr., 44, 147–190.

Guieu, C., Loye-Pilot, M.-D., Ridame, C., and Thomas, C., 2002. Chemical characterization of the Saharan dust end-member: Some biogeochemical implications for the western Mediterranean Sea, J. Geophys. Res., 107(D15). DOI:10.1029/2001JD000582.

Gullu, G.H., Olmez I., Aygun S., Tuncel G., 1998. Atmospheric trace element concentration over the eastern Mediterranean Sea: Factors affecting temporal variability. J. Geophys. Res., 103(2): 943-954.

Herut, B., Krom,M. D., Pan, G., andMortimer, R., 1999: Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: sources, fluxes and possible impact, Limnol. Oceanorg., 44: 1683–1692.

Herut, B., Collier, R., and Krom, M. D., 2002. The role of dust in supplying nitrogen and phosphorus to the Southeast Mediterranean, Limnol. Oceanorg., 47: 870–878.

Herut, B., Zohary, T., Krom, M. D., Mantoura, R. F. C., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T., and Thingstad, T. F., 2005. Response of east Mediterranean surface water to Saharan dust: On-board microcosm experiment and field observations, Deep-Sea Res. Par. II, 52: 3024–3040.

Howarth, R.W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J.A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., Zhao-Liang, Z., 1996. Regional nitrogen budgets and riverine N and P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry 35: 75-139.

Howarth, R.W., Marino, R., 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: evolving views over three decades. Limnol. Oceanogr. 51, 364-376.

Humborg, C., Conley, D.J., Rahm, L., Wulff, F., Cociasu, A., Ittekot, V., 2000. Silicon retention in River basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. Ambio 29, 45-51.

Humborg C., Ittekkot V., Cociasu A. and Bodungen B.V., 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. Nature 386: 385-388.

Ibáñez, J.J., Haïdar-Boustani, M., Al-maqdissi, M., Armendáriz, A., González Urquijo J., Teira L., 2008. Archaeological survey in the Homs Gap (Syria). Campaigns of 2004 and 2005, in J.Mª Córdoba, M. Molist, Mª.C. Pérez, I. Rubio & S. Martínez. (Eds.). Proceedings of the 5th international congress on the archaeology of the ancient Near East, Madrid, 3-8 April 2006: 151-62. Madrid: Universidad Autónoma de Madrid.

Khélifi-Touhami, M., Ounissi, M., Saker, I., Haridi, A., Djorfi, S., Abdenour, C., 2006. The hydrology of Mafragh estuary (Algeria): Transport of inorganic nitrogen and phosphorus to the adjacent coast. J. Food. Agric. Environ. Vol.4 (2): 340-346.

Koçak, M., Nimmo, M., Kubilay, N., and Herut, B., 2004. Spatio-temporal aerosol trace metal concentrations and sources in the Levantine basin of the eastern Mediterranean, Atmos. Environ., 38: 2133–2144.

Krom, M. D., Herut, B., and Mantoura, R. F. C,. 2004. Nutrient budget for the Eastern Mediterranean: implications for P limitation, Limnol. Oceanorg., 49, 1582–1592.

Kubilay, N. and Saydam, C., 1995. Trace elements in atmospheric particulates over the Eastern Mediterranean: concentration, sources and temporal variability, Atmos. Environ., 29: 2289–2300.

Kubilay, N.N., Yemenicioðlu, S., Saydam, A.C., 1995. Airborne material collections and their chemical composition over the Black Sea. Mar. Pollut. Bull., 30: 475-483.

Kubilay, N., Nickovic, S., Moulin, C., and Dulac, F., 2000. An illustration of the transport and deposition of mineral dust onto the eastern Mediterranean, Atmos. Environ., 34: 1293–1303.

Loÿe-Pilot, M. D., Martin, J. M., and Morelli, J., 1986. Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean, Nature, 321: 427–428.

Ludwig, W., Dumont, E., Meybeck, M., Heussner, S., 2009. River discharges of water and nutrients to the Mediterranean and Black Sea: major drivers for ecosystem changes during past and future decades? Prog. Oceanogr. 80: 199-217.

Mariotti, A., Struglia, M.V., Zeng, N., Lau, K.M., 2002. The hydrological cycle in the Mediterranean region and implications for the water budget of the Mediterranean Sea. J. Climate 15: 1674-1690.

Mariotti, A., Ballabrera-Poy, J., Zeng, N., 2005. Tropical influence on Euro-Asian autumn rainfall variability. Clim. Dynam. 24: 511-521.

Markaki, Z., Oikonomou, K., Koc¸ak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., and Mihalopoulos, N., 2003. Atmospheric deposition of inorganic phosphorus in the Levantine basin, eastern Mediterranean: spatial and temporal variability and its role in seawater productivity, Limnol. Oceanorg., 48: 1557–1568.

Markaki, Z., Loÿe-Pilot, M. D., Violaki, K., Benyahya, L., and Mihalopoulos, N., 2010. Variability of atmospheric deposition of dissolved nitrogen and phosphorus in the Mediterranean and possible link to the anomalous seawater N:P ratio, Mar. Chem., 120: 187–194.

Meddi, M.M., Assani, A.A., Meddi, H., 2010. The temporal variability of annual rainfall in the Macta and Tafna catchments, Northwestern Algeria. Water Resour. Manage. 24: 3817-3833. DOI: org/10.1007/s11269-010-9635-7.

Meybeck, M., 2003. Global analysis of River systems: from Earth system controls to Anthropocene syndromes. Phil. Trans. R. Soc. Lond., B 358: 1935-1955.

Meybeck, M., Dürr, H.H., Roussennac, S., Ludwig, W., 2007. Regional seas and their interception of riverine fluxes to oceans. Mar. Chem., 106: 301–325.

Meybeck, M., Dürr, H.H., Vörösmarty, C.J., 2006. Global coastal segmentation and its River catchment contributors: a new look at land–ocean linkage. Global Biogeochem. Cy. 20, GB1S90. DOI:10.1029/2005GB002540.

Milliman, J.D, 2007. Impact of human activities on present-day mediterranean Rivers. Rapp. Comm. int. Mer Médit., 38

Montagna, P.A., Alber, M., Doering, P., Connor, M.S., 2002. Freshwater inflow: science, policy, and management. Estuaries 25: 1243-1245.

Nixon, S.W., 2005. Coastal marine eutrophication: a definition, social causes and future concerns. Ophelia 41: 199-219.

Nixon, S.W., S. B.Olsen, E. Buckley, R. Fulweiler., 2004. Lost to the Tide. The Importance Of Freshwater Flow To Estuaries. Final Report submitted to the Coastal Resources Center. Narragansett, RI: University of Rhode Island, Graduate School of Oceanography. http://www.crc.uri.edu

Ounissi, M, Bouchareb, N., 2013. Nutrient distribution and fluxes from three Mediterranean coastal Rivers (NE Algeria) under large damming. C. R. Geosci., 345: 81–92. DOI: org/10.1016/j.crte.2013.02.002

Ounissi, M., Frehi, H., 1999. Variability of microphytoplankton and Tintinnida (ciliated protozoa) in an eutrophic sector of the Annaba Gulf (S.W. Mediterranean). Cah. Biol. Mar., 40(2): 141-153.

Ounissi, M., Khammar, H., Ziouch, O., Saker, I., Haridi, A., Khelifi-Touhami, M., Abdenour, C., 2008. Apports d'azote et de phosphate au littoral d'Annaba par les effluents urbains, industriels et par la rivière Seybouse (Algérie). In: International Conference on rapid urbanisation and land use conflicts in coastal cities, Chouikhi, A., Zibdah, A., Khalaf, A. (Eds.), INOC, Izmir, Turkey, 13, pp. 181-186.

Pitta, P., Stambler, N., Tanaka, T., Zohary, T., Tselepides, A., Rassoulzadegan, F., 2005. Biological response to P addition in the Eastern Mediterranean Sea: the microbial race against time, Deep-Sea Res. Part II, 52: 2961–2974.

Rabalais, N.N., Turner, R.E., Díaz, R.J., Justic, D., 2009. Global change and eutrophication of coastal waters. ICES J. Mar. Sci. 66(7) : 1528-1537. DOI:10.1093/icesjms/fsp047.

Ragueneau, O., Schultes, S., Bidle, K., Claquin, P. and Moriceau, B., 2006. Si and C interactions in the world ocean: Importance of ecological processes and implications for the role of diatoms in the biological pump. Global Biogeochem. Cy. 20. DOI: 10.1029/2006GB002688.

Ridame, C. and Guieu, C., 2002: Saharan input of phosphate to the oligotrophic water of the open western Mediterranean Sea, Limnol. Oceanorg., 47(3): 856–869.

Seitzinger, S.P., Harrison, J.A., Dumont, E., Beusen, A.H.W., Bouwman, A.F., 2005. Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: an overview of Global Nutrient Export from Watersheds (NEWS) models and their application. Global Biogeochem. Cy. 19, GB4S01. DOI:10.1029/2005GB002606.

Spokes, L.J., Jickells, T.D., 2005. Is the atmosphere really an important source of reactive nitrogen to coastal waters?, Cont. Shelf Res., 25, 2022–2035.

Trigo, R.M., Pozo-Vásquez, D., Osborn, T.J., Castro-Díez, Y., Gámiz-Fortis, S., Esteban-Parra, M.J., 2004. North Atlantic Oscillation influence on precipitation, River flow and water resources in the Iberian Peninsula. Int. J. Climatol. 24, 925–944.

Trigo, R.M., Xoplaki, E., Zorita, E., Luterbacher, J., Krichak, S.O., Alpert, P., et al., 2006. Relations between variability in the Mediterranean region and mid-latitude variability. In: Lionello, P., Malanotte-Rizzoli, P., Boscolo, R. (Eds.), The Mediterranean Climate: An overview of the main characteristics and issues. Elsevier, Amsterdam, pp. 179–226.

Turley, C.M., 1999. The changing Mediterranean Sea-a sensitive ecosystem? Prog. Oceanogr., 44: 387-400.

Turner, R.E., Qureshi, N.A., Rabalais, N.N., Dortch, Q., Justic, D., Shaw, R., Cope, J., 1998. Fluctuating silicate:nitrate ratios and coastal plankton food webs. Proceedings of the National Academy of Sciences USA 95, 13048-13051.

Turner, R.E., Rabalais, N.N., Justic, D., Dortch, Q., 2003. Global patterns of dissolved N, P and Si in large Rivers. Biogeochemistry, 64: 297-317.

Ulbrich, U., Lionello, P., Belušic, D., Jacobeitd, J., Knippertze, P., Kuglitschf, F.G., Leckebuschg, G.C., Luterbacherh, J., Maugerii, M., Maherasj, P., Nissena, K.M., Pavank, V., Pintol, J.G., Saaronim, H., Seubertd, S., Toretih, A., Xoplakif, E., Ziv, B., 2012. Climate of the Mediterranean: Synoptic patterns, temperature, precipitation, winds, and their extremes. In: Lionello, P. (Eds.), The climate of the Mediterranean region-from the past to the future. Elsevier, Oxford, pp. 301-346.

Viaroli, P., Bartoli, M., Giordani, G., Magni, P., Welsh, D.T., 2004. Biogeochemical indicators as tools for assessing sediment quality/vulnerability in transitional aquatic ecosystems. Aquatic Conservation: Marine and Freshwater Ecosystem 14, S14-S29.

Viaroli, P., Giordani, G., Cattaneo, E., Zaldıvar, J.M., Murray, C.N., 2001. Sacca di Goro Lagoon. In: Dupra, V., Smith, S.V., Marshall Crossland, J.I., Crossland, C.J. (Eds.), Coastal and Estuarine Systems of the Mediterranean and Black Sea Regions: Carbon, Nitrogen and Phosphorus fluxes. LOICZ Reports & Studies, No. 19. LOICZ, Texel, The Netherlands, pp. 36-45.

Vörösmarty, C.J., Meybeck, M., 2004. Responses of continental aquatic systems at the global scale: new paradigms, new methods. In: Kabat, P., et al. (Eds.). Vegetation, Water, Humans and the Climate. Springer, Berlin, pp. 375–413.

Walsh, J.J., 1988. On the nature of continental shelves. Academic Press, San Diego.

Chapter I

Coastal environment features

Chapter I: Coastal environment features

1. The Mediterranean Sea

The Mediterranean Sea is the largest quasi-enclosed sea on the earth. It covers about 2.5 million km^2, with an average water depth of about 1.5 km. The drainage basin of the Mediterranean stretches over more than 5 million km^2 (Ludwig et al., 2009). Nutrients and chlorophyll a pools rank the basin as oligotrophic (Krom et al., 1991; Antoine et al., 1995). The Mediterranean Sea is also a site of intense human activities, the impact of which on the marine environment has still to be clearly assessed and quantified. The present Mediterranean Sea is a concentration basin (freshwater loss exceeds freshwater inputs), which forces an anti-estuarine circulation, with saltier and denser water exiting the basin at Gibraltar and a compensating entrance of the fresher Atlantic water (Zavatarelli and Mellor, 1995; Pinardi and Masetti, 2000). The wind stress pattern, the morphology of the basin and the bottom topography produce a somewhat regular pattern in the distribution of eddies and gyres, which are mainly anticyclonic in the southern regions and cyclonic in the northern ones (Pinardi and Masetti, 2000) (Figure 1).

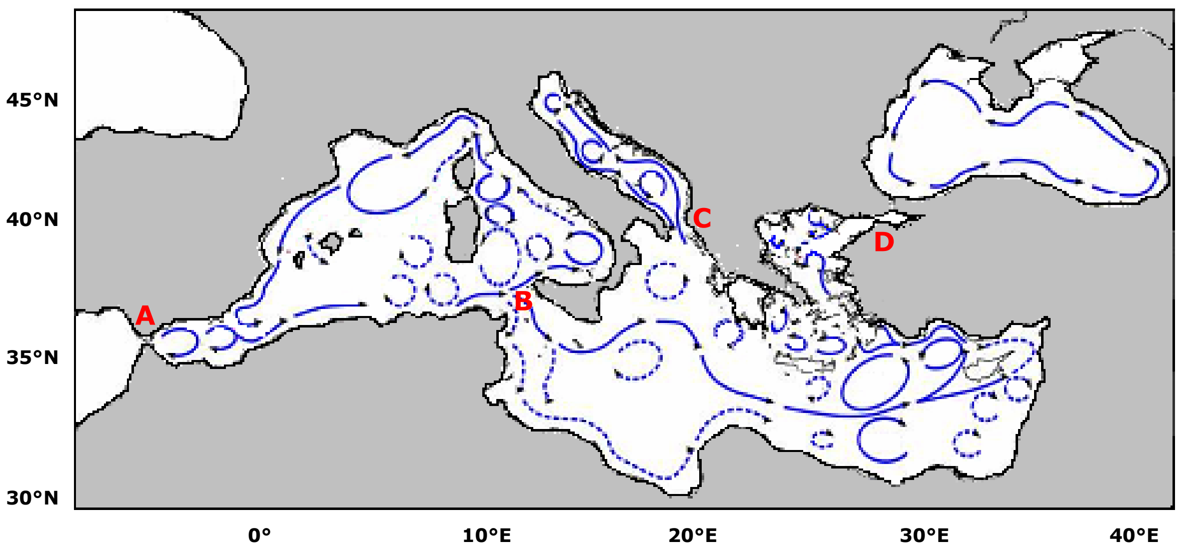

Figure 1: Key traits of surface circulation and connecting straits (A,B,C,D corresponding respectively to: Gibraltar Strait, Cicily Strait, Otranto Strait, Dardanelle Strait) of Mediterranean Sea. (from Siokou-Frangou et al., 2010).

External inputs from the coasts play a significant role in the Mediterranean Sea (Ludwig et al., 2009; Degobbis and Gilmartin, 1990; Cruzado et al., 2002; Moutin et al., 1998). More important at times is the deposition of aerial dust.

Despite the associated uncertainties, budget calculations (Ribera d'Alcala et al., 2003; Krom et al., 2004) suggest that atmospheric inputs support a significant amount of new production. In particular, phosphorus from atmosphere may account for up to 40% of primary production, while nitrogen input may be sufficient for all of the export production in the Mediterranean Sea (Bergametti, 1987; Migon et al., 1989; Guerzoni et al., 1999; Kouvarakis et al., 2001; Markaki et al., 2003). Atmospheric inputs are clearly a crucial factor in the functioning of the basin.

2. The estuaries

An estuary is part of a stream (or River) invaded by the sea at the end of the last glacial period. In macrotidal estuarine system, the sea penetrates several tens to several hundreds of kilometers across the continent and causes a particular hydrodynamics. In microtidal regime, as in the Mediterranean, the intrusion of the sea in the continent is limited. The estuary is thus limited in space and can be ranked as a tidal River. Estuaries may change type due to variations in rainfall and associated River flow. They can also show different characteristics in different sections due to topographic restraints affecting the propagation of the tide along the estuary. The classification of estuaries can be used to describe the variability of salinity of water masses in space and time, classification required legislators and planners. The use of the term estuary to describe a type of moving ecosystem is largely contributed to the development of the so-called "science of estuaries." A very distinct discipline describes unique ecotones environments, ranging as science between oceanography and limnology (Elliot and McLusky, 2002). In the freshwater to ocean continuum, estuaries play a crucial role in influencing the fluxes to coastal waters of the nutrients nitrogen, phosphorus and silica. The range of factors and processes that influence these nutrient fluxes operate over a wide range of time and space scales. Coastal zones, and estuaries in particular, are a focus for human settlement and recent estimates indicate about 40% of the global population lives within 100 km of the shoreline (SEDAC, 2011). Despite being under intense demographic, economic and ecological pressures, estuarine areas provide highly valuable ecosystem benefits for humans (Crooks and Turner, 1999), whilst in the context of global element cycles, riverine inputs are a major source of nutrients to the world ocean (Meybeck 1982; Seitzinger et al., 2010). These inputs must pass through estuaries on their way to the ocean. However the fluxes of nutrients through estuaries may be impacted by a variety of processes (Nedwell et al., 1999).

Estuarine hydrodynamics considers the circulation and mixing within an estuary in response to freshwater inputs via River discharge and injection of saline waters through tidal flows, in addition to heat input during high insolation periods enhancing vertical stratification. If the estuary is large Coriolis effects may also be evident. These factors in combination with morphology lead to varying degrees of vertical stratification, and there is a corresponding classification of estuary based on the type of mixing occurring; highly stratified, partially stratified and well mixed (Dyer, 1973). Kjerfve (1988) and Prandle (2009) provide further information on estuarine physics. Topographic effects can lead to restricted circulation, such as is found in fjordic systems where deep water anoxia or sub-oxia may develop in between periodic flushing events. Additionally extensive salt marsh or intertidal mudflats, such as is found in deltaic systems, may also impact nutrient biogeochemistry. Where River flow is particularly strong, the estuarine mixing zone may extend well beyond the terrestrial limits of a conventional estuary definition and lead to stratified Regions of Freshwater Influence in adjacent coastal waters.

A key hydrodynamic control on biogeochemical processes is the freshwater flushing time of an estuary (Officer and Lynch, 1981), which provides a timescale for the replacement of the freshwater within an estuary by new River water. Flushing times may range from hours or even minutes for small streams entering directly into the sea, to weeks or months in bigger estuarine systems having a large volume (Shen and Wang, 2007). Estuaries host one of the most highly productive marine ecosystems on the planet (Underwood and Kromkamp, 1999), and much of this production is underpinned by the presence of algae. In the water column the growth of phytoplankton is controlled by a range of factors.

3. The Rivers water

In a global context, the continental water cycle plays a decisive role for the climate, ecology and biogeochemistry of the Earth system. However, this cycle is modified by human activities such as irrigation, dams and other needs of the population (Vörösmarty and Sahagian, 2002). On either capital reduction in terrestrial water from 1970 (Shiklomanov, 2000), overall use of water has increased exponentially with the growth of the world population and its economic development. Dams have been built for different purposes (irrigation, hydropower, human consumption), leading to the imprisonment of freshwater flows in the continents instead of reaching their natural environment, the sea. This storage of Rivers water increases evaporation and changes the water budget at the watershed scale and increases the duration of the flow to the sea. 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.

On an ecological point of view, the contribution of Mediterranean Rivers plays a key role in fertilization and productivity of adjacent coasts. However, it is certain that water inputs and associated components (nutrients and sediment) in the Mediterranean have undergone significant changes over the decades in both quantity and quality (Ludwig et al., 2009). Water resources are limited and the pressure on the Rivers becomes particularly important due to the construction of dams and irrigation of agricultural lands (Margat and Treyer, 2004). In addition, Rivers water intercepted in dams increases the particle sedimentation, decreases turbidity, and increases thus the primary production. This leads to the appearance of phytoplankton blooms which sediment leading the diatoms testes faster than other forms of phytoplankton (Humborg et al., 2000). Moreover, before reaching the sea, the continental origin nutrients transiting the aquatic continuum of wetlands, Rivers, estuaries where they are subjected of intense physical, chemical and biological transformations of trapping, removal or retention (Billen et al., 1991; Telesh, 2004). It constitutes therefore a real filter zones (Lisitzin, 1999; Conley et al., 2000) by trapping nutrients and contaminants and transforming materials introduced to the coast. On another ecological plan, direct relations between the importance of freshwater inputs and nutrients that are getting from, the coastal organic production is now well established (Deegan et al., 1986; Budgen et al., 1982; El-Sayed et van Gert, 1995; Estrada, 1996; Tsai et al., 1997, Postel et al., 1998; Daskalov, 1999). The coastal environment can therefore be highly controlled by nutrient enrichment of riverine and estuarine origins.

4. The nutrients

4.1. The 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, 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 (NID) 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 NID in the order of 10% (Aminot and chaussepied, 1984). 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.

4.2. The 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 elements 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 inorganic phosphorus. 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 by product of the chemical leaching which is transported to the sea almost exclusively by Rivers (Meybeck, 1982; Froelich, 1982).

4.3. The 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 River water and estuaries is from weathering of terrigenous rock minerals by naturally acidic rainwater (Drever, 1997). In estuarine and marine systems the dissolved form of silica is silicic acid ($Si(OH)_4$) (Siever, 1971), whilst particulate forms are predominantly detrital quartz, alumino-silicates, 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 are 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:

$$CaAl_2Si_2O8 + \underline{2CO_2} + 8H_2O \rightarrow Ca^{2+} + 2Al(OH)_3 + 2H_4SiO_4 + \underline{2HCO_3}$$

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:

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

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 could be said in fact that "*What Carbon is to biosphere, Silica is to lithosphere*" (Sommer et al., 2006).

5. The impacts of human activities on the chemistry of continental waters and on the coastal functioning and productivity

Over the past decades, human activity has significantly changed the hydrology and chemistry of the waters of Mediterranean Rivers as a result of water retention in dams (Lehner et al., 2011) and important introduction masses of nitrogen and phosphorus from agricultural, industrial and domestic waste (Margat, 2004; EEA, 1999). These massive contributions have a direct impact on the chemistry of surface water, the flow of nutrients to the coast and the functioning of coastal ecosystems (Howarth et al., 1996; Meybeck, 2003; Turner et al., 2003; Nixon, 2003; Liu et al., 2008). Margat and Treyer (2004) highlight the fact that water resources in the Mediterranean are scarce and anthropogenic pressures on Rivers become particularly important. Moreover, the construction of dams on Rivers and water abstraction for irrigation have evolved since the 1960s and have greatly reduced River flow by at least 20%, which has profoundly altered the natural functioning of the Mediterranean Rivers (Ludwig et al., 2009; Humborg et al., 2008). However, nothing is more fundamental to the functioning of a coastal area than the quantities and the timing of fresh water delivery, reported Montagna et al. (2002). In addition, the transfer of nutrients to the sea plays a key role in the hydrological balance of carbon, dissolved nutrients (nitrogen, phosphorus and silicon), sediment and surface water biodiversity (Meybeck, 2003). Despite the key hydrological role they occupied, Rivers are also known to play a special role in supporting the production of the Mediterranean where production areas are limited to adjacent coasts (Bosc et al., 2004). Conjunction with the reduced flows and silicon (Si) retained in large proportions in dams, flux of nitrogen (N) and phosphorus (P) have 3-5 times increased (Meybeck, 2003, Ludwig et al., 2009 ; Dürr et al., 2009) and N:P:Si are thus modified.

Ludwig et al. (2009) reported that the decrease in the Si flux of the Mediterranean Rivers is rather related to the reduced flows of Rivers highly subject to regulation by dams. In parallel, anthropogenic contributions were more than 5 times increase fluxes to the sea of N and P. River inputs of nutrients play a crucial role in the productivity and the functioning of coastal waters. Figure 2 schematically shows the modifications in the chemistry of Rivers due to human activities and their effects on biogeochemistry and functioning of coastal systems.

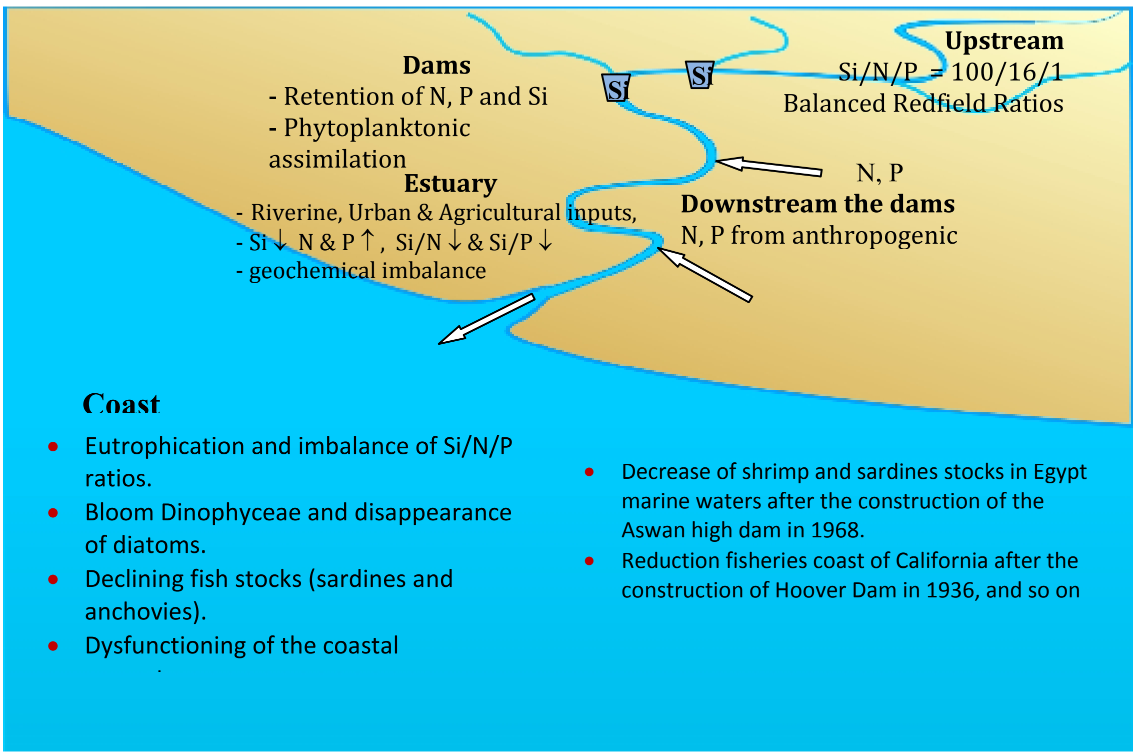

Figure 2: Diagram of the impacts of human activities on the chemistry of continental waters and on the coastal functioning and productivity.

These biogeochemical modifications are responsible for many negative impacts: loss of habitat and biodiversity, increased proliferation of harmful phytoplankton species, eutrophication, and hypoxia (Cloern et al., 2001; Ragueneau et al., 2006; Billen et Garnier, 2007; Howarth et al., 1996; Rabalais, 2002; Rabalais et Turner, 2001; Turner et al., 2003). In the same context, Turner et al. (2003) reported that the decrease in the Si:N ratio causes severe changes in the coastal food web including fisheries. In the Mediterranean, it is admitted that Si can not only reduce productivity, but also induce changes in phytoplankton communities with dominance of non-siliceous harmful species. Similarly, Turner et al. (1998), Turner et al. (2003) and Cloern (2001) demonstrate that the decrease in the abundance of diatoms and copepods in coastal areas is linked to the reduction of Si Rivers inputs. These changes in the composition of phytoplankton affect the entire coastal system including the decline of coastal fishery resources.

Upstream dams in the upper basins as a result of low anthropogenic inputs, water chemistry is not affected and there are balanced Redfield ratios (Si:N:P in the order of 100:16:1). Here, Si is more abundant than nitrogen and it is widely enough to support the needs of diatoms (Si:N $\geq$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 (remaining dependent only on soil leaching) is not compensated at the downstream of dams. The chemistry of estuarine waters introduced to coastal waters is altered with modified Redfield ratios. The Si:N ratio often <1 causes significant impacts on the functioning and productivity of coastal waters. 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, 1981; 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 (1981) 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.

6. References

Aminot, A., Chausspied, M., 1984. Manuel des analyses chimiques en milieu marin, 395p.

Antoine, D., Morel, A., and André, J., 1995. Algal pigment distribution and primary production in the eastern Mediterranean as derived from Coastal Zone Color Scanner observations, J. Geophys. Res., 100: 16193–16209.

Artegiani, A., Bregant, D., Paschini, E., Pinardi, N., Raicich, F., Russo, A., 1997. The Adriatic Sea general circulation, J. Phys. Oceanogr., 27: 1515–1532.

Astraldi, M., Conversano, F., Civitarese, G., Gasparini, G. P., Ribera d'Alcalà, M., and Vetrano, A. 2002. Water mass properties and chemical signatures in the central Mediterranean region, J. Mar. Syst., 33–34: 155–177.

Bergametti, G., 1987. Atmospheric input to the western Mediterranean Sea: geochemical and meterological aspects, Ph.D. thesis, Université Paris. 7, France, 302 pp.

Billen, G., Lancelot, C., Meybeck, M., 1991. N, P, and Si retention along the aquatic continuum from land to ocean. In: Mantoura, R.F.C., Martin, J.M., Wollast, R. (Eds.). Ocean Margin Processes in Global Change. Wiley & Sons, Chichester, pp. 19-44.

Billen, G., Garnier, J., 2007. River basin nutrient delivery to the coastal sea: assessing its potential to sustain new production of non-siliceous algae. Mar. Chem., 106: 148-160.

Bosc, E., Bricaud, A., Antoine, D., 2004. Seasonal and inter-annual variability in algal biomass and primary production in the Mediterranean Sea, as derived from 4 years of Sea WiFS observations. Global Biogeochem. Cy. 18. DOI: 10.1029/2003GB002034.

Bougis, P., 1974. Ecologie du plancton marin, Tome I le phytoplancton. Masson & Cie, Paris, 192p.

Budgen, G.L., Hargrave, B.T., Sinclair, M.M., Tang, C.J., Therriault, J.C. & Yeats, P.A., 1982. Freshwater runoff effects in the marine environment: the Gulf of St Lawrence example. Canadian Technical Reports on Fisheries and Aquatic Sciences, 1078: 1-89.

Cloern, J.E., 2001. Our evolving conceptual model of the coastal eutrophication problem. Mar. Ecol. Prog. Ser. 210: 223-253.

Conley, D.J., 1997. Riverine contribution of biogenic silica to the oceanic silica budget. Limnol. Oceanogr., 42: 774-777.

Conley, D.J., Stalnacke, P., Pitkanen, H., Wilander, A., 2000. The transport and retention of dissolved silicate by Rivers in Sweden and Finland. Limnol. Oceanogr., 45(8): 850-853.

Crooks, S., Turner, R.K., 1999. Integrated coastal management: sustaining estuarine natural resources. In: Fitter A.H., Raffaelli DG. (Eds.), Adv. Ecol. Res., 29. Academic Press, pp. 241–89.

Cruzado, A., 1985. Chemistry of Mediterranean waters. In: Margalef, R. (Ed.), Western Mediterranean. Pergamon Press, Oxford, pp. 126–147.

Cruzado, A., Velàsquez, Z., Pérez, M. C., Bahamon, N., Grimaldo, N. S., Ridolfi, F., 2002. Nutrient fluxes from the Ebro River and subsequent across-shelf dispersion, Cont. Shelf Res., 22: 349–360.

Daskalov, G., 1999. Relating fish recruitment to stock biomass and physical environment in the Black Sea using generalized additive models. Fisheries Research, 41: 1-23.

Deegan, L.A., Day, J.W., Gosselink, J.G., Yáòez-Arancibia, A., Soberȯn, G., Sánchez-Gil, P., 1986. Relationships among physical characteristics, vegetation distribution and fisheries yield in Gulf of Mexico estuaries, in: D.A. Wolfe. (Eds.). Estuarine Variability. Academic Press, New York.

Degobbis, D., and Gilmartin, M., 1990. Nitrogen, phosphorus, and biogenic silicon budgets for the northern Adriatic Sea, Oceanol. Acta, 13: 31–45.

Drever, J.I., 1997. The geochemistry of natural waters:surface and groundwter environments. Lebanon USA: Prentice Hall.

Dürr, H.H., Meybeck, M., Hartmann, J., Laruelle, G.G., Roubeix, G.G., 2009. Global spatial distribution of natural riverine silica inputs to the coastal zone. Biogeosc. Discuss., 6: 345-401.

Dyer, K.R., 1973. Estuaries: a physical introduction. London: John Wiley and Sons.

European Environment Agency EEA., 1999. State and pressures of the marine and coastal Mediterranean environment. Environmental assessment series. Office for Official Publications/EE, L-2985 Luxembourg. 5: 137p.

Elliot, M., and McLusky, D.S., 2002. The need for definition in understanding estuaries. Estuar. Coast. Shelf S., 55: 815-827.

El-Sayed, S.Z., Gert, L.V., 1995. The south-eastern Mediterranean ecosystem revisited: thirty years after the construction of the Aswan high dam, Quarterdeck, 3(1): 4-7.

Estrada, M., 1996. Primary production in the north-western Mediterranean. Scientia Marina, 60(2): 55-64.

Froelich, P.N., Bender, M.L., Luedtke, N.A., Heath, G.R., Devries, T., 1982. The marine phosphorus cycle. Am. J. Sci., 282: 474-511.

Gassman G., 1994. Phosphine in the fluvial and marine hydrosphere. Mar. Chem; 45:197–205.

Gruber, N., Galloway, J.N., 2008. An Earth-system perspective of the global nitrogen cycle. Nature; 451(7176). DOI :10.1038/nature06592

Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loye-Pilot, M. D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., and Ziveri, P., 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea, Progr. Oceanogr., 44: 147–190.

Howarth, R.W., Billen, G., Swaney, D., Townsend, D., Jaworski, N., Lajtha, K., Downing, J.A., Elmgren, R., Caraco, N., Jordan, T., Berendse, E., Freney, J., Kudeyarov, V., Murdoch, P., Zhao-Liang, Z., 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Biogeochemistry, 35: 75-139.

Humborg, C., Conley, D.J., Rahm, L., Wulff, F., Cociasu, A., Ittekkot, V., 2000. Silicon retention in River basins: Far-reaching effects on Biogeochemistry and aquatic food webs in coastal marine environments. Ambio, 29(1): 45-50.

Humborg, C., Smedberg, E., Rodriguez Medina, M., Mörth, C.M., 2008. Changes in dissolved silicate loads to the Baltic Sea and the effects of lakes and reservoirs. J. Mar. Sys., 73: 223-235.

Karageorgis, A., Gardner, W., Georgopoulos, D., Mishonov, A., Krasakopoulou, E., and Anagnostou, C., 2008. Particle dynamics in the Eastern Mediterranean Sea: A synthesis based on light transmission, PMC, and POC archives (1991–2001), Deep-Sea Res. Part. I, 55:177–202.

Karl, D.M., 2000. Aquatic ecology. Phosphorus, the staff of life. Nature, 406:31-33. DOI:10.1038/35017683

Kjerfve, B., 1988. Hydrodynamics of estuaries, Estuarine physics, 1. Boca Raton: CRC Press. 163p.

Kouvarakis, G., Mihalopoulos, N., Tselepides, A., and Stavrakakis, S., 2001. On the importance of atmospheric inputs of inorganic nitrogen species on the productivity of the eastern Mediterranean Sea, Global Biogeochem. Cy., 15: 805–817.

Krom, M.D., Kress, N., Brenner, S., Gordon, L., 1991. Phosphorous limitation of primary productivity in the Eastern Mediterranean Sea, Limnol. Oceanogr., 36: 424–432.

Krom, M.D., Herut, B., and Mantoura, R.F.C., 2004. Nutrient budget for the Eastern Mediterranean. Implications for phosphorus limitation. Limnol. Oceanogr., 49: 1582–1592.

Le Gal, Y., 1989. Biochimie marine. Ed. Masson, Paris, 222p.

Lehner, B., Reidy Liermann, C., Revenga, C., Vorosmarty, C., Fekete, B., Crouzet, P., Doll, P., Endejan, M., Frenken, K., Magome, J., Nilsson, C., Robertson, J.C., Rodel, R., Sindorf, N., Wisser, D., 2011. Global Reservoir and Dam Database, Version 1 (GRanDv1): Reservoirs, Revision 01, http://sedac.ciesin.columbia.edu/data/set/grand-v1- reservoirs-rev01.

Lisitzin, A.P., 1999. The continental-ocean boundary as a marginal filter in the World Oceans. In: Gray, J.S., Ambrose, J.r.W., Szaniawska, A. (Eds.). Biogeochemical Cycling and Sediment Ecology. Kluwer Academic Publishers, Dordrecht, pp. 9-103.

Liu, K.K., Seitzinger, S., Mayorga, E., Harrison, J., Ittekkot, V., 2008. Fluxes of nutrients and selected organic pollutants carried by Rivers, Chapter 8 in: E. Urban & S. Greenwood. (Eds.). PACKMEDS - Dynamics and vulnerability of semi-enclosed marine systems: the integrated effects of changes in sediment and nutrient input from land. Scientific Committee on Progress in the Environment (SCOPE), New York, pp 141-167.

Ludwig, W., Dumont, E., Meybeck, M., Heussner, S., 2009. River discharges of water and nutrients to theMediterranean and Black Sea: Major drivers for ecosystem changes during past and future decades?, Prog. Oceanogr., 80: 199–217**.**

Malanotte-Rizzoli, P., Manca, B., Ribera d'Alcalà, M., Theocharis, A., Bergamasco, A., Bregant, D., Budillon, G., Civitarese, G., Georgopoulos, D., Korres, G., Lascaratos, A., Michelato, A., Sansone, E., Scarazzato, P., Souvermezoglou, E., 1997. A synthesis of the Ionian Sea hydrography, Circulation and water mass pathways during POEM phase I, Prog. Oceanogr., 39 : 153–204.

Margat, J., 2004. L'eau dans le basin méditerranéen : situation et prospective. Les fascicules du Plan Bleu. MAP Technical Report Series No. 158, Athena, 366p.

Margat, J., Treyer, S., 2004. L'eau des méditerranéens: situation et perspectives. Plan Bleu PNUE/PAM, Sophia-Antipolis.

Markaki, Z., Oikonomou, K., Kocak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., Mihalopoulos, N., 2003. Atmospheric deposition of inorganic phosphorus in the Levantine Basin, eastern Mediterranean: Spatial and temporal variability and its role in seawater productivity, Limnol. Oceanogr., 481: 557–1568.

Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world Rivers. American Journal of Science, 282: 401–50.

Meybeck, M., 2003. Global analysis of River systems: from Earth system controls to Anthropocene syndromes. Phil. Trans. R. Soc. Lond. B 358: 1935-1955.

Migon, C., Copin-Montégut, G., El egant, L., and Morelli, J., 1989. Etude de l'apport atmosphérique en sels nutritifs au milieu côtier méditerranéen et implications biogéochimiques, Oceanol. Acta, 1218: 7–191.

Millot, C. 1999. Circulation in the Western Mediterranean Sea, J. Mar. Syst., 20: 423–442.

Monaghan, E.J., Ruttenberg, K.C., 1999. Dissolved organic phosphorus in the coastal ocean: reassessment of available methods and seasonal phosphorus profiles fromthe Eel River Shelf. Limnol. Oceanogr., 44: 1702–14.

Montagna, P.A., Alber, M., Doering, P., Connor, M.S., 2002. Freshwater inflow: Science, policy and management. Estuaries, 25: 1243-1245.

Moutin, T., Raimbault, P., Golterman, H. L., and Coste, B., 1998. The input of nutrients by the Rhone River into the Mediterranean Sea: recent observations and comparison with earlier data, Hydrobiologia, 373: 237–246.

Nedwell, D.B., Jickells, T.D., Trimmer, M., Sanders, R., 1999. Nutrients in estuaries. In: Fitter, A.H., Raffaelli, D.G. (Eds.). Adv. Ecol. res., 29. Academic Press, pp. 43–92.

Nixon, S.W., 2003. Replacing the Nile: are anthropogenic nutrients providing the fertility once brought to the Mediterranean by Great River? Ambio, 32: 30-39.

Officer, C.B., Lynch, D.R., 1981. Dynamics of mixing in estuaries. Estuar. Coast. Shelf S., 12: 525-533.

Pinardi, N., Masetti, E., 2000. Variability of the large scale general circulation of the Mediterranean Sea from observations and modelling: a review, Palaeogeogr., Palaeoclimatol., Palaeoecol., 158: 153–173.

PNUE/P.b., 2003. Les menaces sur les sols dans les pays méditerranéens. Sophia Antipolis, Plan Bleu, ISBN : 2-912081-13-0., 70p.

Prandle, D., 2009. Estuaries: dynamics, mixing, sedimentation and morphology. Cambridge University Press.

Postel, S.L., Morrison, J.I., Gleick, P.H., 1998. Allocating fresh water to aquatic ecosystems: the case of the Colorado River delta. Water Int., 23: 119-125.

Rabalais, N.N., 2002. Nitrogen in aquatic ecosystems. Ambio, 31: 102-112.

Rabalais, N.N., Turner, R.E., 2001. Coastal hypoxia. Coastal Estuary Studies 52. Washington DC: American Geophysical Union.

Ragueneau, O., Tréguer, P., Anderson, R.F., Brzezinski, M.A., 2000. Understanding the silicon cycle in the modern ocean: a prerequisite for the use of biogenic opal as a paleoproductivity proxy. Global Planet Change, 26: 317-365.

Ragueneau, O., Conley, D.J., Leynaert, A., Longphuirt, S.N., Slomp, C.P., 2006. Responses of coastal ecosystems to anthropogenic perturbations of silicon cycling. In: Unger, D., Humborg, C., Tac, A.D.N., Ittekkot, V. (Eds.), The silicon cycle. Human Perturbations and Impacts on aquatic systems. Scientific Committee on Problems of the Environment (SCOPE) Series 66, p296.

Redfield, A.C., 1958. The biological control of chemical factors in the environment. American Science, 46: 205-222.

Ribera d'Alcalà, M., Civitarese, G., Conversano, F., and Lavezza, R. 2003. Nutrient fluxes and ratios hint at overlooked processes in the Mediterranean sea, J. Geophys. Res., 108, 8106. DOI:10.1029/ 2002JC001250.

Rousseau, V., Leynaert, A., Daoud, N., Lancelot, C., 2002. Diatom succession, silicification and silicic acid availability in Belgian coastal waters (southern North Sea). Mar. Ecol. Progr. Series, 236: 61-73.

Ruttenberg, K.C., 2003. The global phosphorus cycle. In: Schlesinger WH, editor. Treatise on geochemistry, 8. Elsevier; p. 585–643.

SEDAC., 2011. CSD coastal population indicator: data and methodology page. Socioeconomics and data and applications center. http://sedac.ciesin.columbia.edu/es/csdcoastal.html

Seitzinger, S.P., Mayorga, E., Bouwman, A.F., Kroeze, C., Beusen, A.H.W., Billen, G., et al., 2010. Global River nutrient export: A scenario analysis of past and future trends. Global Biogeoch. Cy., 24.

Shen, J., Wang, H.V., 2007. Determining the age of water and long-term transport times cale of the Chesapeake Bay. Estuar. Coast. Shelf S., 74: 585–98.

Shiklomanov, I.A., 2000. World water resources and water use: Present assessment and outlook for 2025. In: Rijsberman FR, ed. World Water Scenarios. London: Earthscan, pp. 160-203.

Siever, R., 1971. In: Wedepohl KH, editor. Handbook of geochemistry. Berlin: Springer-Verlag, p. 442.

Siokou-Frangou, I., Christaki, U., Mazzocchi, M.G., Montresor, M., Ribera d'Alcalà, M., Vaqué, D., Zingone, A., 2010. Plankton in the open Mediterranean Sea: a review. Biogeosciences, 7: 1543–1586.

Sommer, M., Kaczorek, D., Kuzyakov, Y., and Breuer, J., 2006. Silicon pools and fluxes in soils and landscapes. J. Plant. Nutr. Soil. Sci., 169: 582-582.

Telesh, I.V., 2004. Plankton of the Baltic estuarine ecosystems with emphasis on Neva Estuary: a review of present knowledge and research perspectives. Mar. Pollut. Bull., 49: 206-219.

Tréguer, P., Nelson, D. M., van Bennekom, A. J., DeMaster, D. J., Leynaert, A., Quéguiner, B., 1995. The silica balance in the world ocean: a reestimate. Science, 268: 375-379.

Tsai, C.F., Chen, P.Y., Chen, C.P., Lee, M.A., Shiah, G.Y., Lee, K.T., 1997. Fluctuation in abundance of larval anchovy and environmental conditions in coastal waters off south-western Taiwan as associated with the El Niňo southern oscillation. Fish Oceanogr., 6: 238-249.

Turner, R.E., Qureshi, N., Rabalais, N., Dortch, Q., Justic, D., Shaw, R.F., Cope, J., 1998. Fluctuating silicate: nitrate ratios and coastal plankton food webs. Prog. Nat. Sci. 95: 13048-13051.

Turner, R.E., Rabalais, N., Justic, D., Dortch, Q., 2003. Global patterns of dissolved N, P and Si in large Rivers. Biogeochemistry 64: 297-317.

Underwood, G.J.C., Kromkamp, J., 1999. Primary production by phytoplankton and microphytobenthos in estuaries. Adv. Ecol. Res., 29: 93-153.

Vörösmarty, C.J., Sahagian, D., 2000. Anthropogenic disturbance of the terrestrial water cycle. BioScience, 50(9): 753-765.

Wahby, S.D., Bishara, N.F., 1980. The effect of the River Nile on Mediterranean water, before and after the construction of the High Dam at Aswan. In: River inputs to ocean systems. pp. 311-318, UNESCO/IOC/UNEP.

Wedepohl, K.H., 1995. The composition of the continental crust. Geoch. Cosmoch. Acta., 59(7): 1217-1232.

Wollast, R., Mackenzie, F.T., 1983. The global cycle of silica, in: Silicon geochemistry and biogeochemistry, edited by: Aston, S. E., Academic Press, London, pp. 39-76.

Yool, A., Toby Tyrrell, T., 2003. Role of diatoms in regulating the ocean's silicon cycle. Global Biogeoch. Cy., 17(4). DOI: 10.1029/2002GB002018.

Zavatarelli,M. and Mellor, G. L. 1995. A numerical study of the Mediterranean Sea circulation, J. Phys. Oceanogr., 25: 1384–1414.

Chapter II

Sites and samplings

Chapter II: Sites and samplings

1. Sampling sites

1.1. Environmental context and anthropogenic inputs in the Annaba Bay

1.1.1. Weather conditions

The study area is subject to a Mediterranean climate, characterized by the presence of two distinct periods. A wet period extending from September to April and the other dry between May and August. This type of climate encouraged by high slope and poor vegetation cover in Mediterranean region will have a significant influence on the hydrological regime of surface water (Loup, 1974). The average monthly temperature in the region is about 17°C where the interval varies between 9.2°C (January and February 2005) to 25.6°C (July). Overall, the average monthly temperature fluctuations coincide with those found in the waters of Seybouse and Mafrag estuaries (Haridi, 2010). The catchments of the Annaba Bay are among the wettest ones in the country (500 to 900 mm). This, strongly influence both the hydrological regime of the estuaries and the receiving shelf of Annaba. The majority of the rainfall distribution during the wet season promotes an excess of water, while during the hyper-dry months (July and August), the region has a considerable water deficit. Such contrast will affect the water balance and flow regime of surface waters.

Under the northerly winds, the Mistral and Tremonton actions, the water cool in winter, while it heats in summer under the influence of the south wind (Sirocco). Haridi, (2010) reported that the intensity of the wind varied only between 2.8 and 5.7 m s^{-1} with an average of 3,8 m s^{-1}.

1.1.2. Anthropogenic inputs

- **The urban waste of the western Annaba city**

Domestic wastewater consist of physiological inputs, various contributions (sewage, solid waste discharged into toilet), and water to domestic use (basin, bath and shower, dishwasher). Physiological inputs are mainly feces and human urine. About 30-45 kg of wet fecal matter is produced per person per year, or 10-15 kg of fecal dry matter (Lentner et al., 1981).

An inhabitant as an individual generates every day a certain amount of domestic pollution. This is why it is defined the concept of inhabitant equivalent which corresponds on average to 166 grams per day per capita of pollutants (Barroin, 1991) divided into 57g d^{-1} oxidizable materials, 90g d^{-1} of suspended solids, 15 g d^{-1} of nitogen, 4g d^{-1} phosphate.

Previous works (Laabed, 2006) provided the first observations on the largest urban effluent of the city of Annaba. It is an open flowing emissary on a path of about 4 km and leads to the sea shores of the Seybouse city, Annaba (Fiigure 3).

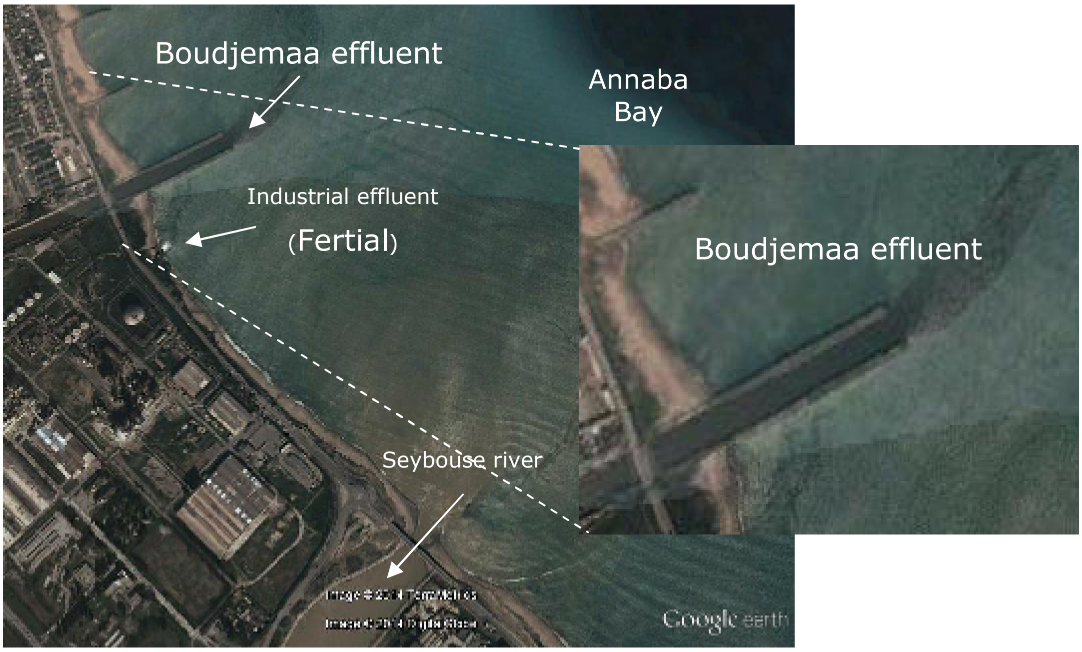

Figure 3: Site position of the urbain waste of the western Annaba city in Annaba Bay.

These works aimed to describe the domestic wastes composition in nutrients and their inflowing into the coastal waters. This effluent discharged nearly 700 t yr^{-1} of P-PO_4, and a comparable amount of dissolved inorganic nitrogen (DIN).

Boudjemâa effluent, the major wastewater entering the Bay, crosses the western plain of Annaba city and runs up to the sea (Figure 3). Before reaching the sea, the effluent receives multiple domestic sewages from several sewer lift stations and many other connections to domestic sewages (Figure 4). It is estimated that the effluent brings the domestic wastes of about 100,000 inhabitants. Outside the riverine water, the effluent had a flow varying generally within the day between 0.2-1 m^3 s^{-1}. But it is ultimately a real wastewater outfall.

Figure 4: Views of Boudjemâa effluent in winter and spring. Top: discharges of FERTIAL sewer in Boudjemâa effluent. Below: Boudjemâa effluent outlet.

Data from Khammar (2007) showed that most of DIN discharged to the Bay is as $N\text{-}NH_4$ (78%), with an annual flow of about 160 tons corresponding to an average daily flow of 435 kg d^{-1}. Mean winter values reached 1,67 kg d^{-1}, which represented three times the annual average (Table 1). This is linked to the effluent flow bringing additional loads from storm water originating from the north-eastern watershed part.

Nitrites discharges are also important especially in winter and spring with average daily flow of 100 kg d^{-1} (Table 1). The average annual flow is about 18 t yr^{-1}. Similarly, the largest flow of nitrates occurs in winter with a seasonal average of 229 kg d^{-1}. The values as high as 663 kg d^{-1} are observed in December 2006. Not only the richness of waters that increase in nitrate flows but also the high effluent flow in this rainy time of year. Nitrate flux nevertheless remained little important (13%) in front of the quantities discharged in reduced nitrogen (Table 1). It is estimated that the introductions to the coast in that element of oxidized nitrogen is in the range of 20 to 30 t yr^{-1}.

More generally, it is understood that the amounts of DIN released into the Bay are considerable (560 kg d^{-1}) as shown in table 1. These quantities of enriching materials but also very polluting will certainly impact the receiving environment.

Table 1: Average daily flux (kg d^{-1}) in each season of the nitrogen transported to the Bay by Boudjemâa effluent during the year 2006. The percentage (%) of the reduced fractions is also given. DIN: dissolved inorganic nitrogen (Khammar, 2007).

Flux	Winter	Spring	Summer	Autumn	average
N-NH_4 (kg d^{-1})	880	360	277	225	435
N-NO_2 (kg d^{-1})	108	86	1,9	0,6	49
N-NO_3 (kg d^{-1})	229	63	4	7,7	76
NID (kg d^{-1})	1 217	510	283	233	560
% NH_4	72	71	98	96	78
P-PO_4 (kg d^{-1})	748	331	327	250	400

The urban effluent discharges to the Bay enormous amounts of PO_4 (Table 1), especially in winter. Nearly the half (46%) of P-PO_4 is introduced into the Bay during the winter. Considering the relative constancy of an urban discharge in terms of phosphorus, it may be noted that the half of the transfer comes undoubtedly from the contributions of the watershed.

- **The industrial waste (FERTIAL)**

The chemical industry is one of the most water consumer sectors in particular for the production of chemical fertilizers for agricultural use. The complex FERTIAL of Annaba, used daily over 1 Million m^3 of water (Saker, 2007). Overall, the fertilizer industry produces some 360 million fertilizer products, equivalent to nearly 140 million tons of nutrients. In Algeria, FERTIAL group is specialized in the production, marketing and development of fertilizers, ammonia and derivatives. Group (FERTIAL, 2004) had annual production capacity:

- 1 million tons of ammonia
- 825,000 tons of ammonium nitrate
- 240,000 tons of UAN
- 800,000 tons of phosphate fertilizers (all forms combined).

FERTIAL convey effluents from water processing and by-products from the manufacture of chemical fertilizers and sanitary ($Ca(H_2PO_4)_2$; P_2O_5, K_2O; $NP_2O_5K_2O$; NH_4NO_3; NH_3, etc.). The wastewater delivery flow is substantially constant, about 1 million m^3 d^{-1}.

The seawater used is pumped from the seaport area (Figure 5). These releases also contain some amounts of ammonia which was initially destined to be delivered as atmospheric emissions. This effluent was regularly surveyed from January to December 2006 at the point of discharge into the sea (Figure 6). In addition to the main sewer, there are other minor discharges with a flow varying between 0.2-0.5 $m^3\ s^{-1}$. These minor sewers that bring several compounds of phosphorus and nitrogen, were also followed for the period January to December 2006. The flow of this industrial effluent is remarkably constant and do not exceed 0.5 $m^3\ s^{-1}$ (Figure 6).

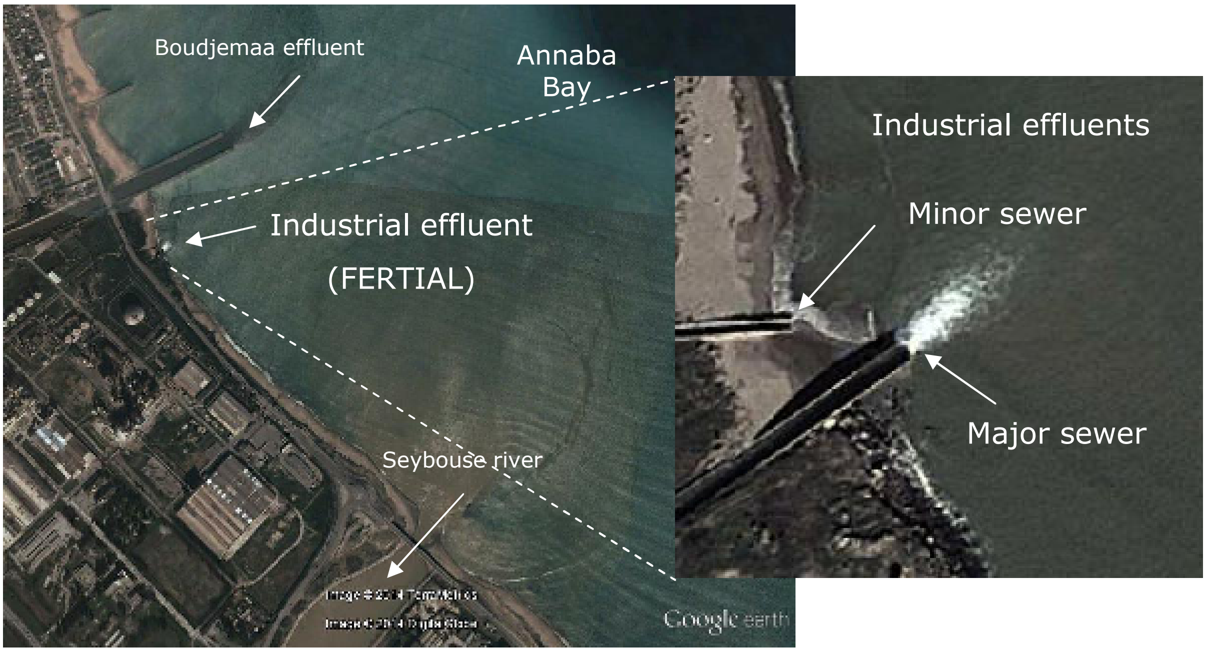

Figure 5: Sites position of major industrial sources of pollution in Annaba Bay: the major and minor sewer of FERTIAL.

These industrial effluents deliver directly into the Annaba Bay without treatment (Figure 5) which induce local eutrophication (Ounissi et al., 1998. Ounissi and Frehi 1999; Frehi, 1995).

The major sewer is highly concentrated in NH_4, compared to other forms of dissolved nitrogen (Table 2). Although, the waters are not regularly loaded with NH_4 where the loads were ranged from 6 to 7,900 kg d^{-1}. This effluent evacuated daily 2 tons on average and represents 93% of discharges of NH_4 (Table 2). In terms DIN, the major sewer delivered about 87% of direct FERTIAL discharges.

Figure 6: Views of FERTIAL industrial unit discharges. Top: Minor sewer. Bottom: Major sewer.

The minor sewer of FERTIAL had lower loads in NH_4, 150-506 kg d^{-1} (Table 2). Loads of NH_4 for the total industry inputs fluctuated in the range of 53-7,980 kg d^{-1}. The flux of the nitrate ions due to FERTIAL discharges are in the order of 268 kg d^{-1}.

Table 2: Average daily flow (kg d^{-1}) of nitrogen transported to the Bay by the major and minor sewer of FERTIAL industry during the year 2006. DIN: dissolved inorganic nitrogen. (Saker, 2007)

	Major sewer	Minor sewer	Total
N-NH_4 (kg d^{-1})	2 045	150	2 195
N-NO_2 (kg d^{-1})	47	9	56
N-NO_3 (kg d^{-1})	268	84	352
DIN (kg d^{-1})	2 360	243	2 603
% NH_4	87	62	84
P-PO_4 (kg d^{-1})	367	79	446

In term of P-PO_4, the major sewer introduced directly into the Bay about 367 kg d^{-1}, but the minor sewer delivered in average 79 kg d^{-1}. The FERTIAL industry by-product delivers daily into the Bay about 0.5 ton of P-PO_4.

1.2. The Seybouse estuary

Seybouse River has a vast watershed 6,500 km² (ABH, 2002) hosting about 1.5 million inhabitants. It includes two important dams with a storage capacity of 400 million m^3 and several weirs retaining about 7.5 million m^3 (Figure 7). These constructions retain approximately half the total annual runoff. Land use in the watershed is being mainly occupied by intensive agricultural practices, and heavy industrial activities are limited to the maritime lower catchment (more than 70 factories, the most important are grouped on maritime Seybouse). According to ABH (2002) the sewerage network is 1,200 km with a connection rate of 80%.

Figure 7: Map of the Seybouse basin showing the two dams built on Charef and Bouhamdane branches. The major agglomerations and cities in the watershed are also represented.

Except during the winter wet season, when Rivers discharge freshwater into the Bay, the Seybouse function as tidal estuary, with large seasonal fluctuations of its salt wedge penetration. The saltwater wedge in the reach 8 km (data not presented). The estuarine salt wedge that occurring in dry years causes strong stratification, in which the freshwater layer occupies less than 20 % of the entire water column.

The flow of the River Seybouse varies greatly according to precipitation on the watershed, which receives from 450 to 735 mm/yr, depending on sub-basins. The LCHF (1976) estimated an annual average flow of about 15 m^3 s^{-1}. An example of the Seybouse flow is provided in figure 8.

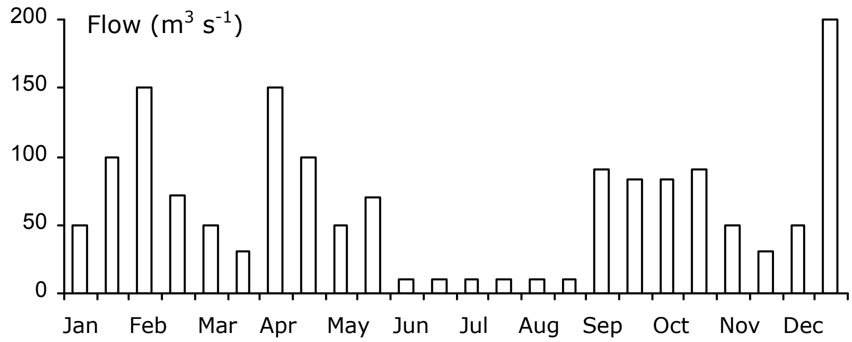

Figure 8: Example of monthly variations of the average flow of Seybouse River during 2003 (after Ounissi et al., 2008).

1.3. The Mafragh estuary

The catchment of Mafragh includes Cheffia and Mexa dams, which are constructed respectively on Bounamoussa and El Kebir branches (Figure 9). Bougous dam is being built closely to Mexa dam in the El Kebir sub-Basin. The estimated flow downstream of the dams of 42 years was in the order of 7 and 5 m^3 s^{-1} respectively for El Kebir and Bounamoussa (Labar, 2003). Unfortunately, these studies did not consider the estuarine portion representative of more than 25% length the of Rivers Estuaries course.

The Mafragh watershed (3,200 km²) is moderately populated (354,000 inhabitants. Agriculture is essentially intensive where irrigation is assured largely by the tributaries of the estuary. The industry in the region is limited to small agro-alimentary factories. The watershed is largely forested in the upper part and includes large marshland in lower part. Between, these parts raise some villages, in the large floodplain, where the activities of the population are mainly subsistence agriculture. Such singular land-use makes the Mafragh watershed among the pristine and virgin area in the Mediterranean region.

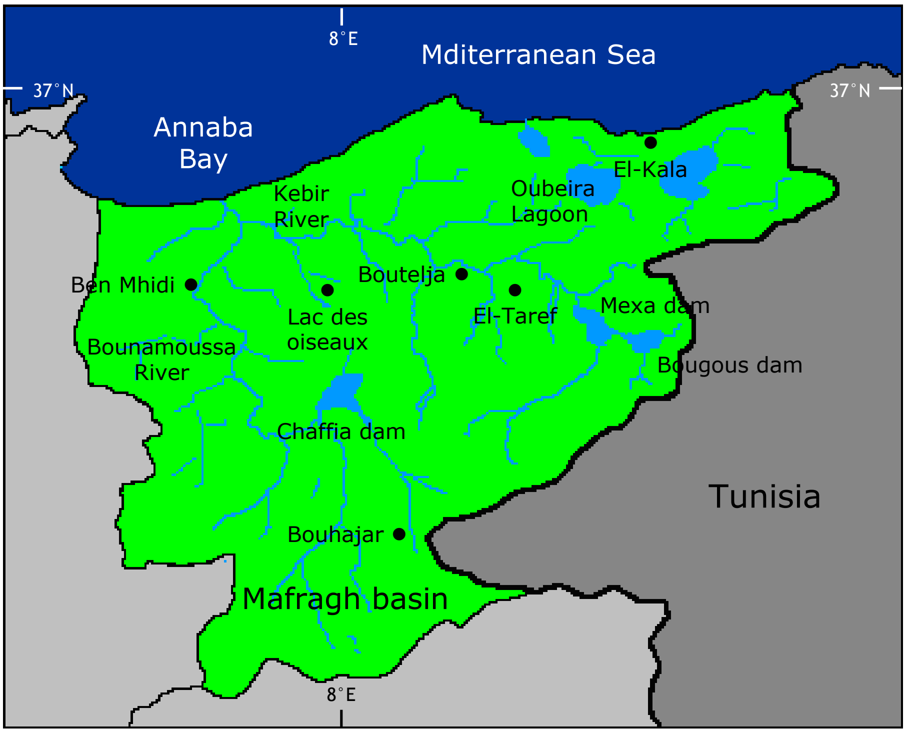

Figure 9: Map of the Mafragh basin representing the hydrographic network of Mafragh system and its branches Bounamoussa and El-Kebir and the three dams: Chafia, Mexa and Bougous. The major agglomerations and cities in the watershed are also represented.

The Mafragh appears as atypical estuary with the hydrologic cycle comprising River phase, estuarine core phase and lagoonal phase (Khélifi-Touhami et al., 2006). The duration of each phase may strongly vary with the River input and the duration of dry season (Figure 10, Figure 11). The Mafragh estuary's mouth might be closed from its tidal connection under extended period of dry years. Following periods of high rainfall (winter and in the beginning of spring) and freshwater runoff, the volume of the estuary is entirely discharged into the sea, and the salt wedge is then retreated to the coast in a few days. From the middle spring to the end of autumn, the estuary is dominated by tidal advection, and expands in a very stratified system, with two layers (Figure 10, Figure 11), in which the saltwater layer occupies over 80% of the water column.

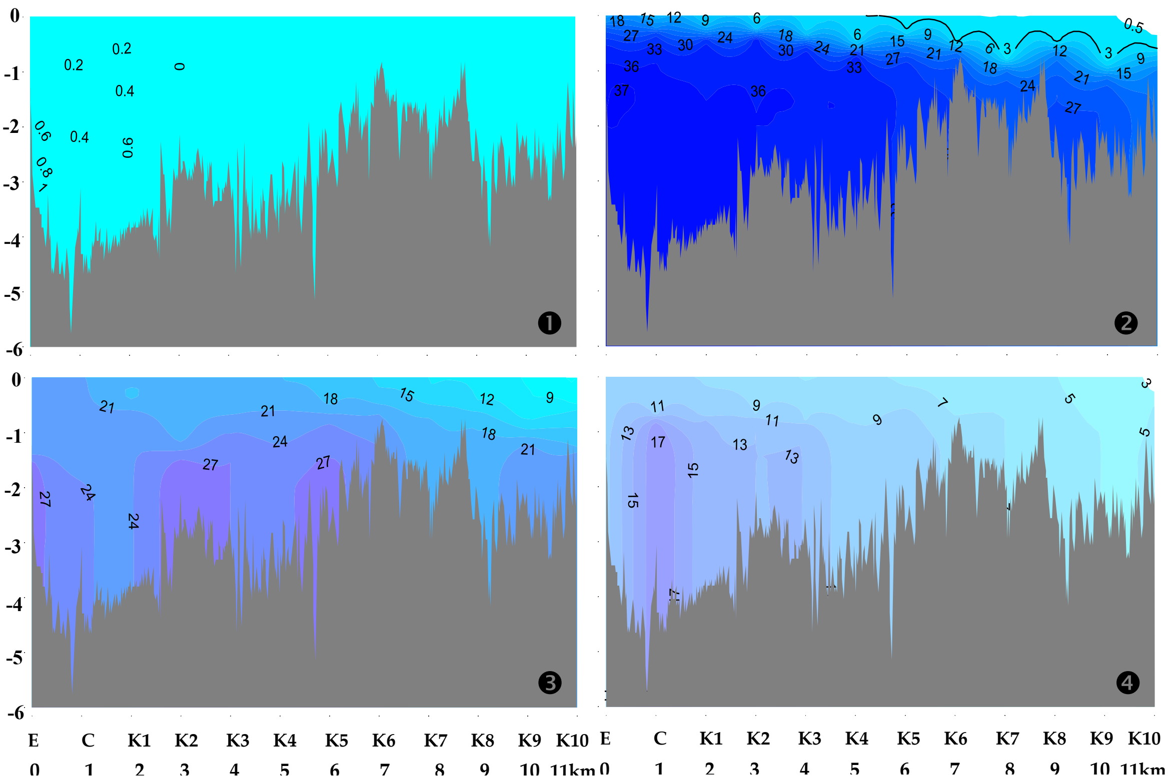

Figure 10: Salinity profiles (pss) for the Mafragh estuary (Kebir western branch) in 2006, from the mouth (M), the confluence (C) of the two tributaries (Kebir western and Bounamoussa) up to 11 km inland (K1–K11). 1: winter, 2: spring, 3: summer, 4: autumn.

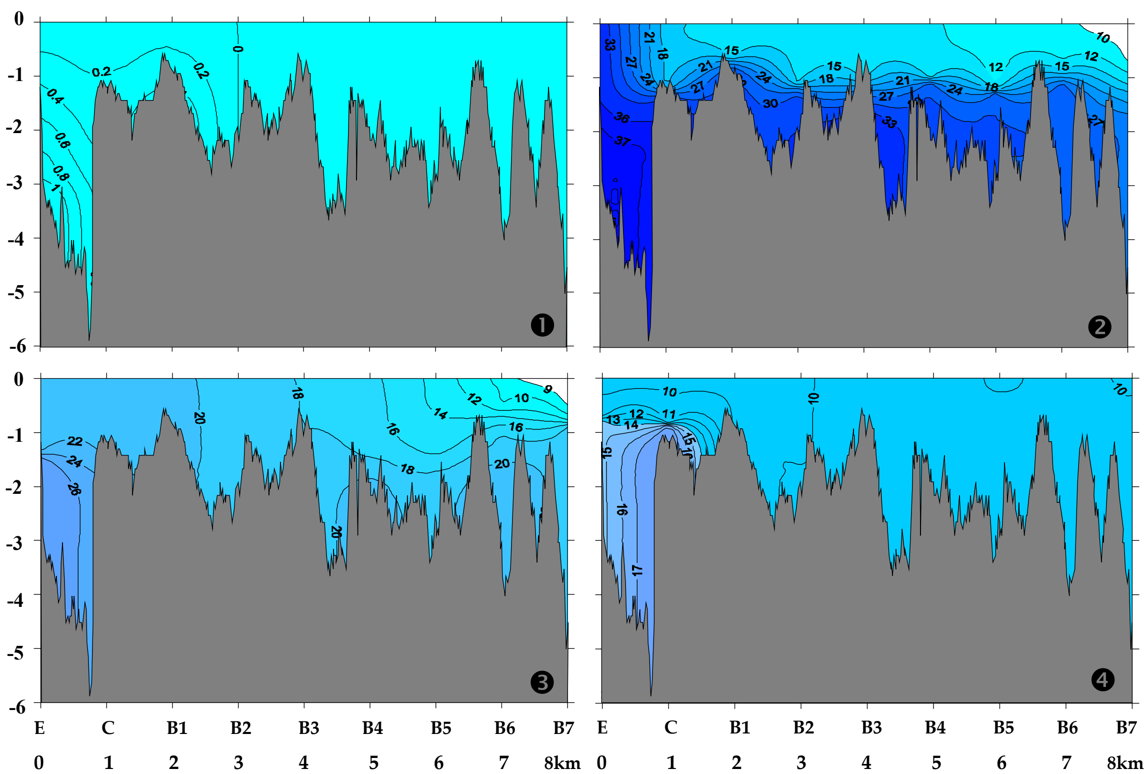

Figure 11: Salinity profiles (pss) for the Mafragh estuary (Bounamoussa branch) in 2006, from the mouth (M), the confluence (C) of the two tributaries (Kebir western and Bounamoussa) up to 7 km inland (B1–B7). 1: winter, 2: spring, 3: summer, 4: autumn.

Water flow is strongly variable with extreme values: 0 $m^3 s^{-1}$ in dry period up to 300 $m^3 s^{-1}$ during flooding periods. Average annual precipitation in the watershed is up to 800 mm and evaporation is about 1,250 mm. The Mafragh region is one of the most important underground water reserve of Algeria. The salt wedge extends to 20km inland on the El-Kébir River and 15km inland on the Bounamoussa River. The estuary is generally temporary opened in winter and spring except in heavy rainfall year where it is still opened all the year. Mean depth in Bounamoussa branch reaches 2.3m and 3m for El-Kébir branch. The two estuaries have a comparable surfaces and volumes and forms together about 3-4 Millions m^3 with a total water surface of about 120 ha.

The main fish species captured are the European Eel, Sea bass, Mullets and Carps. As a wetland site, the mafragh hydrosystem receives over 50 species of immigrant birds; among them the Duck (*Anas penelope*) population reaches 2,000 individuals in winter. The Mafragh estuarine system is an important crossing site for many marine young fish species (mullets, Eel, sea bass) which can reach and populate the contiguous Rivers, Marshland and the Oubeira lake (Figure 9).

1.4. The precipitation sampling sites

Our study is limited to Annaba region (Figure 12) which extends for about 450 km² and centred particularly on the rural and urban areas of Annaba. The climate varies slightly from the north to the south, from a sub-humid domain to a semi-arid domain, but in a general way, the Mediterranean climate prevails, humid and temperate, characterized by a mild winter and hot summer with fairly weak water resources (rain, hail and snow) the snow usually makes its appearance on the massive high altitudes. The Monthly precipitations in Annaba region during the study period (2011-2013) are given in table 3.

Table 3: Monthly precipitation in Annaba region during the study period (2011-2013). Data are from the meteorological station of Annaba.

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
2011	55.62	112.53	84.83	57.4	41.65	23.63	3.05	0	37.6	104.38	55.12	86.63
2012	34.04	169.4	51.05	50.3	3.31	0.51	1.02	0	53.08	64.27	35.81	69.85
2013	115.85	124.98	55.13	47.76	16.77	0	0	21.08	39.38	17.27	231.14	44.2

Rain water samples were collected from the Annaba region including Annaba city, Berrahal, Sidi Ammar, Kherraza, Chetaibi, Chbaita mokhtar, El-Bouni. Geographic Characteristics of the studied points are presented in table 4.

Table 4: Geographic Characteristics of the studied points.

Point	Positionning
Treat	36°55'57.46' N 7°30'54.64' E
Berrahal	36°49'59.07' N 7°27'44.16' E
Chetaibi	37°03'53.60' N 7°22'46.73' E
Sidi-Amar	36°48'59.92' N 7°42'52.20' E
El Bouni	36°50'20.94' N 7°39'49.43' E
Chebaita	36°27'57.52' N 7°44'26.00' E
Annaba	36°53'5O.75' N 7°44'07.61' E

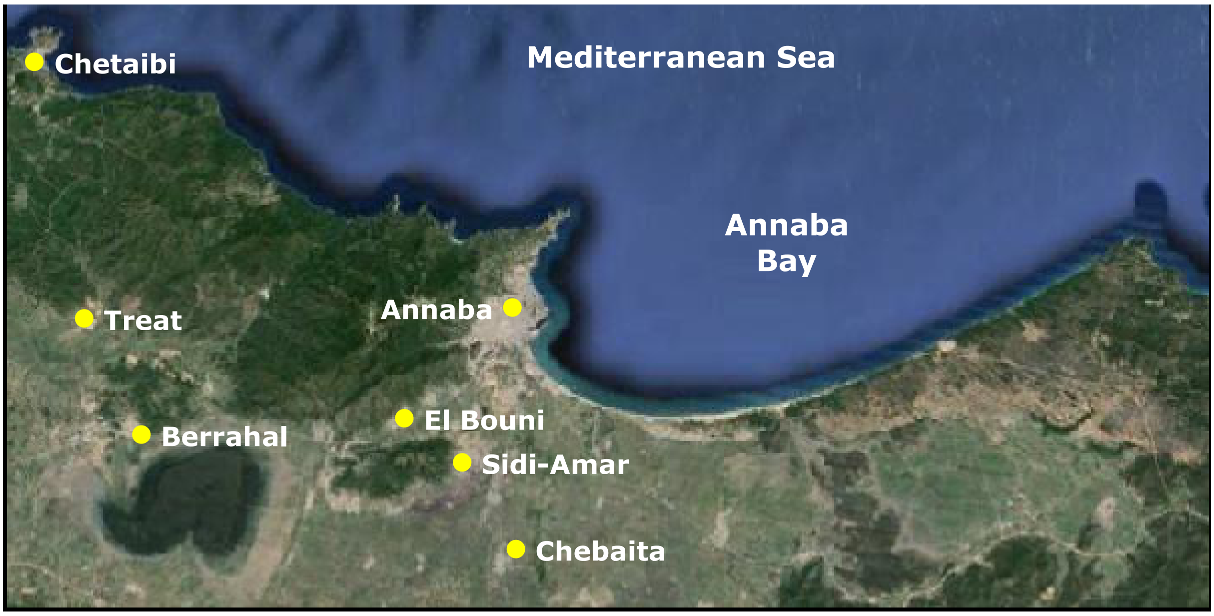

Figure 12: Precipitation sites position in urban and rural areas in the Annaba region.

1.5. The Bay

In the Bay of Annaba, the modified Atlantic water current (MAW) moves eastward from the marine side (Millot and Taupier-Letage, 2005) and crosses the shelf of Annaba (Figure 9), which allows some renewing of the outer neritic waters (Ounissi and Fréhi, 1999). However, the inner part of the Bay mostly influenced by continental inputs from the Seybouse and the Mafragh estuaries (Figure 13) and urban waste of about one million people in the city of Annaba and its surrounding villages. Moreover, industrial waste from a single large fertilizer factory delivered over a million m^3 d^{-1} heavily loaded with nitrogen and phosphorus compounds.

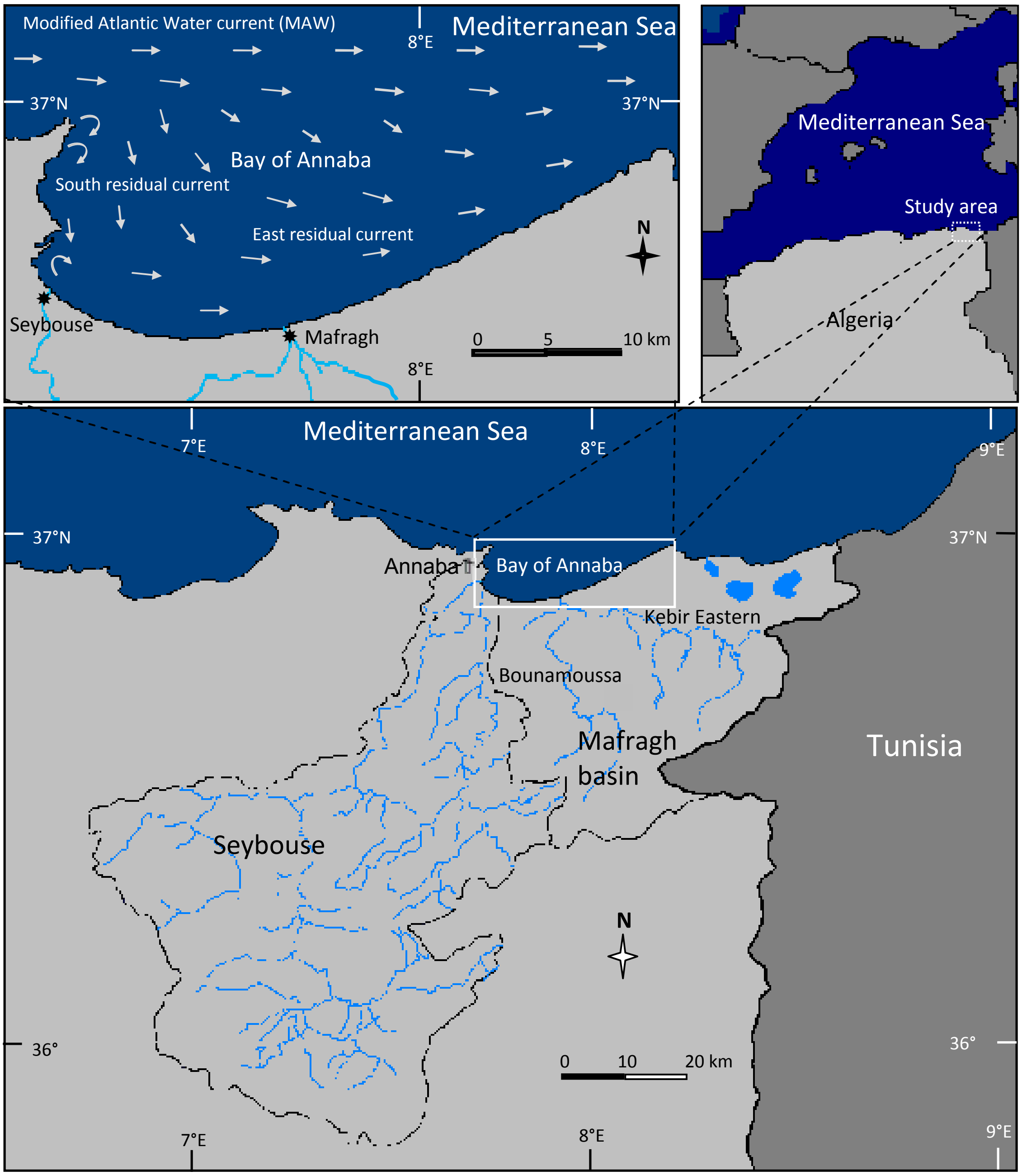

Figure 13: Map of the Bay of Annaba and its drainage basin formed by the Seybouse and Mafragh basins.

It can be learned from the works of Fréhi, 1995; Khélifi-Touhami, 1998 and Ounissi et al., 1998 the following remarks:

- The Bay of Annaba has a maximum depth of 100m with an average of 60m; its perimeter is about 100 km and an area of 400 km^2. The Bay of Annaba receives discharges from Seybouse and Mafragh Rivers which drain together a surface of about 9700 km^2.
- The speed values ranged between 10 and 35 cm s^{-1}. Current direction is from north to east (270° to 90°). Seaward, the current of a north-easterly direction, gradually changes direction near the coast where it flows eastward. At the entrance of the Gulf (Cap de garde), there is the usual direction of circulation in South-western Mediterranean (Algeria current).
- The nitrate ions are particularly abundant in the south-east part where concentrations fluctuate between 5 and 67 µM and are ordered according to a strong gradient coast wide (South - North). Similarly, the phosphate ions are abundant too and their mean levels amounted to 2-18 µM. The average values of the N:P ratio (1.4 to 3.5) indicate the existence of a situation of intensive eutrophication which extends over almost the entire year.
- The phytoplanktonic chlorophyll *a* concentrations are always high even in winter and averaged between 3.6 and 10.5 mg m^{-3}. Such contents express a situation of phytoplanktonic eutrophication.

However, data of Ziouch (2007) indicate that the western sector of Annaba Bay, adjacent to Mafragh estuary, is considerably rich in organic matter (POC & DON) where concentrations were on average 500 times higher than those in the open sea. This richness represents only half of phosphate, DIN, POC and 1:6 of Chl *a* values of the adjacent estuary. These values situated Annaba Bay among the eutrophic coastal environment. Moderate values of Chla (1.5 mg m^{-3} on average) indeed express this state of the coastline richness.

2. Sampling and analytical methods

2.1. The estuaries

Surface water samples were taken in the estuaries' outlets monthly from January 2007 to December 2009. As we collected water samples, we also measured the flow velocity from the outlet' stations of the Seybouse and Mafragh estuaries with CM-2 current meter, Toho Dentan Co.Ltd, Tokyo. Water salinity and temperature measurements were taken with a multi-parameter probe, WTW 197i. As mentioned by the manufacturer, the precisions of the salinity and the temperature measurements are respectively ± 0.1 pss and ± 0.1 °C. The flow rate (m3 s^{-1}) was calculated by multiplying the water velocity (m s^{-1}) by the total surface area (m^2) of a transect of the estuary' at the outlet' stations. However, the estimation of the freshwater inputs from highly dynamic and atypical estuarine systems was not easy to carry out. This suggests some explanations.

For example, the estuarine part varies with the season from 0 to 7 km in the Seybouse River estuary, and from 0 to 20 km in the Mafragh River estuary (Figure 14). If we measure nutrient concentrations and water discharge at 7 km in the Seybouse River estuary, where the salinity is near 0 pss (fresh water), we estimate here what is introduced to the estuary. By the opposite, when we determine water discharge at the mouth, we always measure what is introduced to the sea from the estuary in dry season and from the River in wet season. The problem now is how to estimate the amount of the fresh water discharged, from the estuary, into the sea in such highly dynamic systems. The tide in the estuaries is semidiurnal and microtidal, where the ebb and flood phases duration vary largely. Depending on River flow in particular, the flood phase fluctuates between 0 and 6 h, and the ebb tide one varies between 6 and 24 h (but the discharge may continue for several days because the tide regime is masked by high River flow). The other constraint is the depth of the fresh water layer. We determine at each sampling the periods of the tidal phase, and the fresh water layer as can be seen in figure 14. The measurements of salinity were taken vertically each 10 cm. For example, in May (purple 1 circle), the freshwater layer is about 45 cm; April: 190 cm (black circle); August: 0 cm (blue circle), and so on (Figure 14). Having the current velocity, the freshwater layer, the ebb tide phase duration, we can determine the estuarine inputs.

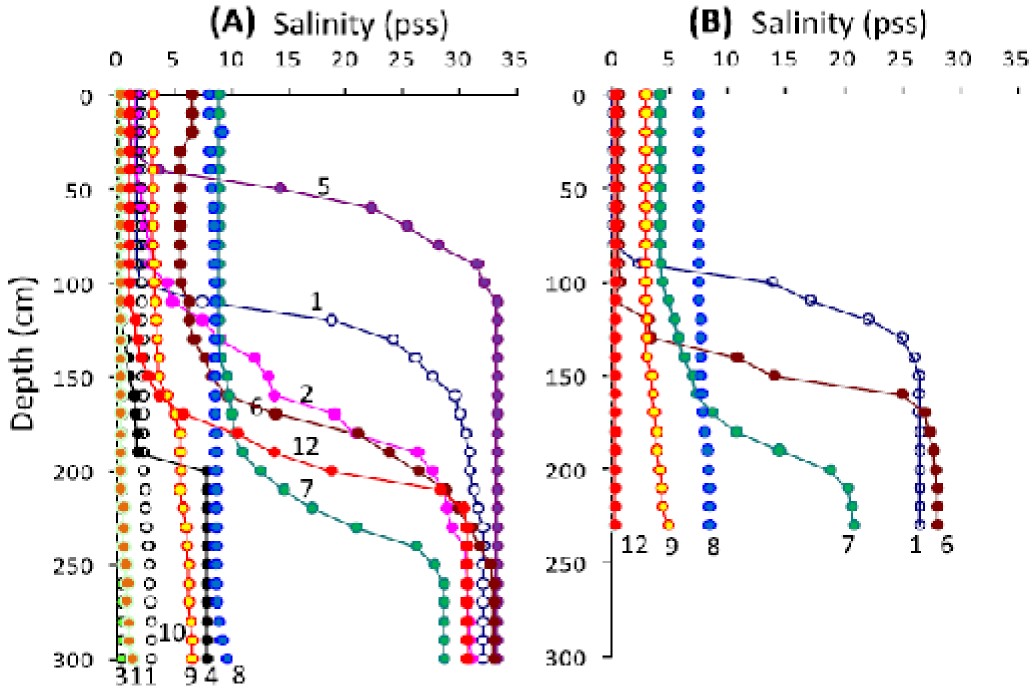

Figure 14: Monthly vertical profiles of salinity at the outlet (A) and at 11 km from the outlet (B) of the Mafragh estuary (Kebir eastern branch), during the year 2007. 1-12 correspond successively to the salinity profiles of January to December.

The Seybouse estuary was only sampled twice in the years 2008 and 2009. In the laboratory, after filtration of the sample through a Whatman GF/C glass filter (0.5 µm porosity), all nutrient (phosphate: PO_4; ammonium: NH_4; nitrate: NO_3; nitrite: NO_2; silicic acid: $Si(OH)_4$) concentrations were determined by means of the standard colorimetric methods described by Parsons et al. (1989). Their precisions are: ± 3 % (PO_4), 5% (NH_4), 3 % (NO_3), 2.5 % (NO_2), 2.5 % ($Si(OH)_4$).

The instantaneous flux of nutrients was calculated by multiplying their levels by the estuary flow. The annual loads for nutrients were estimated using the method of average instantaneous loads (Preston et al., 1989):

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

where F is the annual load (tons/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.

2.2. The Bay

Sites for spatial data were selected by purposive sampling using maximum variation technique (Scherer, 1984). On the shelf of Annaba, three sampling stations were chosen (Figure 15) according to the importance of external influences: the coastal area submitted to the Seybouse estuary plume (Inner Bay, station B1, 6 m depth); the coastal area near the Mafragh estuary (inner Bay, station B2, 19 m depth) and the central Bay far from continental influence and mostly subject to the MAW intrusion (outer water, B3, 40 m depth). To assess the influence of estuarine inputs, the Seybouse and the Mafragh estuaries were sampled at their respective outlet stations (Figure 15).

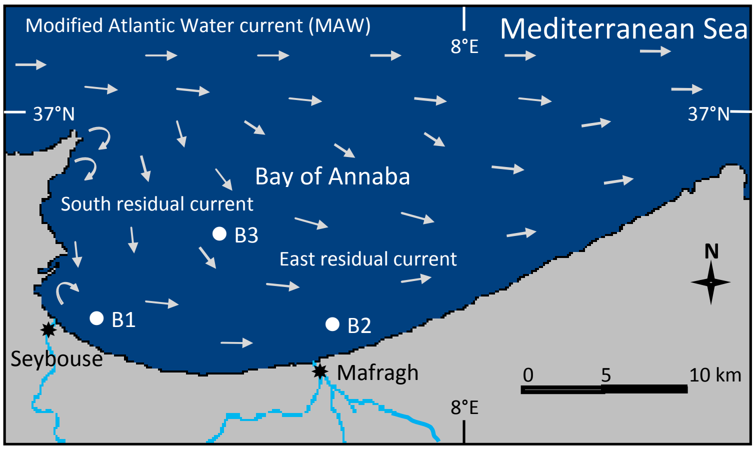

Figure 15: Map of the Bay of Annaba showing the sampling sites located at the estuaries' mouths.

Two liters of water from the middle of the flow were collected for nutrient analysis. Surface water samples were taken from March 2007 to December 2009 in the Bay of Annaba. Due to bad weather in the Bay of Annaba, we were unable to collect several samples: May 2007; March; September and November 2008; and September 2009. In addition to surface water sampling in the Bay of Annaba, bottom waters were sampled using Niskin bottle. Water samples for nutrient analyses were frozen in polyethylene bottles and processed within two days of collection. Nutrient analyses were performed as for estuaries water.

2.3. The wet atmospheric deposition

Rain water sampling was carried out at a rural and urban sites located on the coastline of Annaba region. The seventh sampling sites are not under direct influence of any industrial activities. Sampling of rainwater was performed occasionally during the period October 2011 - May 2013 with our own rain gauge. A transparent plastic bottle whose shape is cylindrical as uniformly as possible is chosen (Figure 16). A bottle with a diameter of about eight centimeters is a minimum.

Figure 16: Rain gauge sampler used in the Annaba region during the period 2011-2013.

The bottle decapitated will be the pluviometer itself. The section of the neck is reversed to make a funnel that will be deposited into the opening (to reduce evaporation). In this particular model, the diameter of the collector funnel is identical to the diameter of the graduated cylinder (1:1) (Figure 16).

The rain gauge is roughly calibrated: a mark on the perfectly cylindrical portion of the bottle is made, and then a second mark, one centimeter above. Then the amount of water needed to change the level from the first to the second mark is measured. The amount thus established is then used for calibration. For example, if you took 150 ml to fill the space between the two brands, depositing a first in the 150 ml empty bottle and mark the level reaches "10 mm" with an indelible pencil. Repeat the operation to mark "20 mm", then "30 mm", and so on. Ideally, the readings after each rainfall will be taken once a day to once again, to avoid evaporation. After each specific event, the rain water sample was immediately transferred into the laboratory for filtration and nutrients analysis.

To cover a representative precipitation area in the Annaba region, 7 stations were chosen (Figure 12) including urban and rural sites. This strategy allows comparing the anthropogenic effect on the chemistry of precipitation in the whole region (urban and rural sites). Also, it can be kept in mind that the Bay of Annaba is under precipitation of both urban and rural areas.

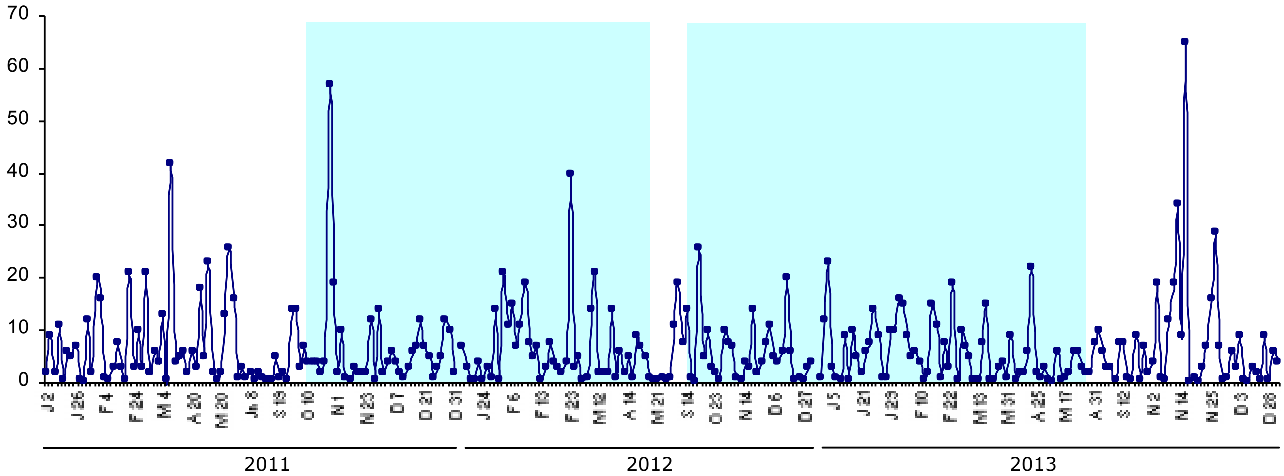

Figure 17: Precipitation days during the study period 2011-2013. Sampled and analyzed rainy days are presented in blue color.

Nutrients were analyzed during the study period in the seven sampling points. These nutrients were analyzed as for estuaries and seawater methods. The nutrient fluxes from wet atmospheric deposition were calculated as for estuarine inputs. However, K is not constant but varies with the number of rainy days of a given year (Table 6). To estimate the received flux by the Bay of Annaba, we have assumed its surface to be around 400 km². At every rain event we have computed the volume received in the Bay by multiplying the rain height (mm) by its surface (400 km²).

Not all rainy days were unfortunately sampled (Figure 17, Table 6). For these lucking samples, we have considered their concentrations, for a given nutrient, to be the mean of urban and rural rain in the corresponding season (Table 5). The deduced values of each nutrient are the average of about 104 samples, we have previously analysed.

Table 5: Seasonal mean (± standard error) of nutrients (µM) in urban and rural rainwater during the period 2011-2013. DIN: dissolved inorganic nitrogen.

	Autumn (D=33)	Winter (D=59)	Spring (D=28)	Summer (D=1)
NH_4	12,2 (± 1.86)	14,1 (± 1.52)	14,2 (1.77)	6,8
NO_3	16,3 (± 2.63)	9,1 (0.69)	8,2 (1.45)	3
NO_2	2,6 (± 0.45)	1,1 (0.14)	0,8 (± 0.12)	6,8
NID	31,1 (± 4.08)	24,3 (1.76)	23,2 (± 2.28)	16,6
PO_4	0,8 (± 0.08)	0,8 (0.07)	1,3 (0.20)	0,5
SiO_4	10,7 (± 1.72)	6,2 (± 0.82)	12,2 (± 2.03)	4,6

Table 6: The rainy (http://www.tutiempo.net/en/Climate/) and sampled days in the study period 2011-2013. Bold values indicate the sampling days. *: > 1 rainwater sample for these dates.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
2011	2. 3. 4. 12. 13. 22. 23. 26. 27. 28. 30.	1. 2. 3. 4. 15. 18. 19. 21. 22. 23. 24. 25. 27. 28.	1. 2. 3. 4. 5. 16. 17. 19. 21. 22.	20. 21. 23. 24. 26. 27.	19. 20. 21. 22.	1. 5. 6. 7. 8. 14.	14. 25.		1. 3. 4. 19. 20. 25. 27. 28.	8. 9. 10. 15. **16**. 21. **24**. **29***. **30***. **31**.	**1***. 2. 3. 6. **16***. **17**. **18**. **23***. **24***. 25. **26***. **28**. **29***. 30.	1. 7. 8. **13**. **16***. **17***. **18***.**19***. **20***. **21**. **22***. **23***. **24***. **26***. **27***.**28**. **29***. **30***. 31.
2012	**3***. 4. 5. **6.** 8. 15. 24. 29. 30. 31.	1.**3***. **4***. **5***. **6**. 7. 8. 9. 10. **11**. 12. **13***. **14**. 15. 16. 17. 18. **20**. **21***. **22***. **23***.	**4**. **6*.** **7***. **8***. **9**. **10***. **11**. 12. 30. 31.	**4*.** **5*.** **6***. 7. **13*** **14*.** **15*.** **16*.** **17*.** **18**.	19. 20. 21. 26.	4.	12.	**31 ***	**1. 2**. 3. **13***. 14. 15. 27.	**12*.** **13**. **14**. **15***. 16. **21***. **22***. 23. 27. **28***. 29.	**5. 6***. 7. 8. 12. **14.** 16. **17.** **19*. 20*.** **21. 22**. **27. 28*.**	**2***. 3. **4*.** **5. 6. 7. 8***. 9. 12. 13. **16**. 22. 27. 30. 31.
2013	1**. 2*.** **3. 4***. 5. 14. **15.16 *.17*.** **18*.** 19.**21 *.22***. **23*.** **24*.** **25*.** 26.27. **28.**29	**2. 3**. 4. **5***. **6*.** **7*. 8*.** **9. 10.** 11. **12*.** **13.** 14. 15. **21***. **22**. **23**. **24**.26.	**1*.** **2***. **3**. 7.**10**. **12***. **13***. **14***. 15. 16. 21. 25. 26. 31.	**1*.** 2. **5. 6.** 7. 8. 21. **23.** **24*.** 25. 27. 30.	1. 2. 15. 16. 17. **22.** 23.			19. 28. 29. 30. 31.	1. 2. 4. 6. 9. 10. 12. 20.	5. 6. 7. 31.	1. 2. 5. 6. 10. 11. 12. 13. 14. 15. 17. 19. 20. 23. 24.25. 26. 27. 28.29.	1. 2. 3. 5. 21.22. 23. 26.27. 28. 30. 31.

2.4. Statistical analysis

Even though purposive sampling offers a substantial amount of information relative to the sampling effort, all estimators are subject to significant bias including correlation, mean, variance, etc. (Scherer, 1984). In fact, the stations have been placed to collect data at strategic points (outlets and their marine plumes and the outer marine station affected by the MAW current) or to find possible gradients. The intentional placement of the stations may be responsible for correlations between nutrients and spatiotemporal variability, but these factors have not been considered in this work. However, data issued from purposive sampling can reveal interesting findings when used in multivariate factorial analyses, especially in environmental diagnosis and to find trends along spatial gradient of the variables (Scherer, 1984).

A correspondence analysis (CA) multivariate technique was then used to determine any possible co-variation between inorganic nutrients and their ratios, both in the estuaries' outlets and at the coastal stations, during the three years of surveys. The CA has several advantages compared to multivariate techniques such as principal component analysis (PCA), and it is more appropriate for the data we collected. Presenting the variables and objects together in a biplot graphic, facilitates the interpretation of the cloud points and their associations. In addition, the CA is a double principal component analysis on the variables (columns) and objects (rows) and also compares rows or columns using the Chi-square distance, which offers a superior method of weighting the individual data. In addition, the data do not need to be normalized, a procedure that can distort reality as it does for PCA (Dervin, 1988). The statistical software Statistica, 2008 was used to perform the CA. The contingency table analyzed with CA is a matrix of the annual averages of 8 nutrient levels and ratios (variables) observed on 15 spatiotemporal situations (objects) representing the two outlets and three coastal stations over three years of survey (2007-2009).

3. References

Agence de Bassins hydrographiques Seybouse-Mellag-constantinois (ABH)., 2002. Bassin de la seybouse. Actualisation. Les cahiers de l'agence, 7 : 32p.

Barroin G., 1991. La réhabilitation des plans d'eaux*, la Recherche*, 238(22) : 1412-1422.

Dervin, C., 1988. Comment interpréter les résultats d'une analyse factorielle des correspondances? ITCF-INAPG, Paris.

Fréhi H., 1995. Etude de la structure et du fonctionnement du système phytoplanctonique dans un écosystème marin côtier : Eutrophisation de la Baie d'Annaba. Thèse de Magister, Université Badji Mokhtar-Annaba, Algérie, 160p.

Haridi, A., 2010. Étude écologique de l'estuaire du Mafragh: Distribution des masses d'eaux, des matières nutritives minérales et organiques (Nord Est D'Algérie). Thèse de doctorat, Université Badji Mokhtar-Annaba.

Khammar, H., 2007. Caractères chimiques des effluents urbains introduits au littoral d'Annaba. Mémoire de Magister, Université Badji Mokhtar-Annaba, 46p.

Khelifi-Touhami, M. 1998. Composition et abondance du zooplancton dans les eaux côtières de l'Est Algérien (Secteur eutrophie du golfe d'Annaba et plateau continental d'El-kala) .Thèse de Magister, Université Badji Mokhtar-Annaba, 132p.

Khelifi-Touhami M., Ounissi M., Saker I., Haridi H., Djorfi S. & Abdennour C., 2006. The hydrology of the Mafrag estuary (Algeria): Transport of inorganic nitrogen and phosphorus to the adjacent coast. Journal of food, Agriculture and Environment, 4(2): 340-346.

Laabed, S. 2006. Transport de phosphate et d'azote par les rejets urbains et industriels au littoral d'annaba. Mémoire de Magister, université Badji Mokhtar-Annaba, Algérie, 40p.

Labar, S., 2003. Contribution à l'identification des aires inondables et qualité physicochimiques des eaux stagnantes temporaires dans la vallée de la Mafrag (Extrême Nord Est Algérien). Thèse magister en Hydrochimie, département de géologie, Université Badji Mokhtar-Annaba, 111p.

Laboratoire Central d'Hydraulique de France (LCHF), 1976. Extension du port d'Annaba: synthèse de l'étude générale des conditions naturelles dans le golfe d'Annaba. LCHF, Maisons-Alfort, 50p.

Lentner C., Wink A., 1981. Units of measurement, body fluids, Composition of the body, Nutrition. Geigy Scientific tables. Ciba-Geigy, Basle.

Loup J., 1974. Les eaux terrestres (hydrologie continentale). Masson et Cie (Ed). Paris: 171pp.

Millot, C., Taupier-Letage, I., 2005. Circulation in the Mediterranean Sea. In: Saliot, A. (Ed.), The Handbook of Environmental Chemistry 5(K). Springer-Verlag, Heidelberg, pp. 29-66.

Ounissi M., Fréhi H., Khélifi-Touhami M., 1998. Composition et abondance du zooplancton en situation d'eutrophisation dans un secteur côtier du golf d'Annaba (Algérie). Analyse de l'institut océanographique, Paris, 73(1): 53-67

Ounissi M., Fréhi H., 1999. Variabilité du microphytoplancton et des Tintinnides d'un secteur hautement eutrophe du golfe d'Annaba (Algérie). Cah. Biol. Mar., 40 : 141-153.

Parsons, T.R., Maita Y., Lalli, C. M., 1989. A manual of chemical and biological methods for sea water analysis. Pergamon Press, 173 p.

Preston, S.D, Bierman, J.R.V.J., Silliman, S.E., 1989. An evaluation of methods for the estimation of tributary mass loads. Water Resour. Res. 25(6): 1379-1389.

Saker, I., 2007. Caractères chimiques des effluents industriels directs introduits au littoral d'Annaba. Mémoire de Magister, Badji Mokhtar-Annaba. 38p.

Scherrer, B., 1984. Biostatistique. Ed. Boucherville, Gaëtan Morin.

Ziouch, O.R., 2007. Hydrologie et biogéochimie du complexe estuarien du Mafrag et de ses panaches littoraux. Mémoire de Magister, Université Badji Mokhtar-Annaba, 54p.

Chapter III

Continental inputs and wet atmospheric deposition

Chapter III: Continental inputs and wet atmospheric deposition

1. The estuaries

1.1. Hydrology at the estuaries' outlets

The hydrological parameters recorded in the two estuaries are given in the figure 18. The estuarine water flow at the respective outlets varied according to the precipitation, especially for the Seybouse estuary, where discharges in 2009 were 6-fold higher than those of 2008 (Figure 18a). Because of the large marshland supplying the Mafragh estuary, discharges varied less and seem to be more important than those of Seybouse (Figure 18b). In the Mafragh the inter-annual variability was mitigated, and did not exceed 4-fold because the surrounding wetlands regulate flow. As seen in the figure 18, the minimum flow was recorded in 2008 because of the low rainfall, as it was for the Seybouse basin. The water temperature varied in the same range in both estuaries, but the annual average value of Seybouse waters was significantly higher because of the amount of wastewater from human population.

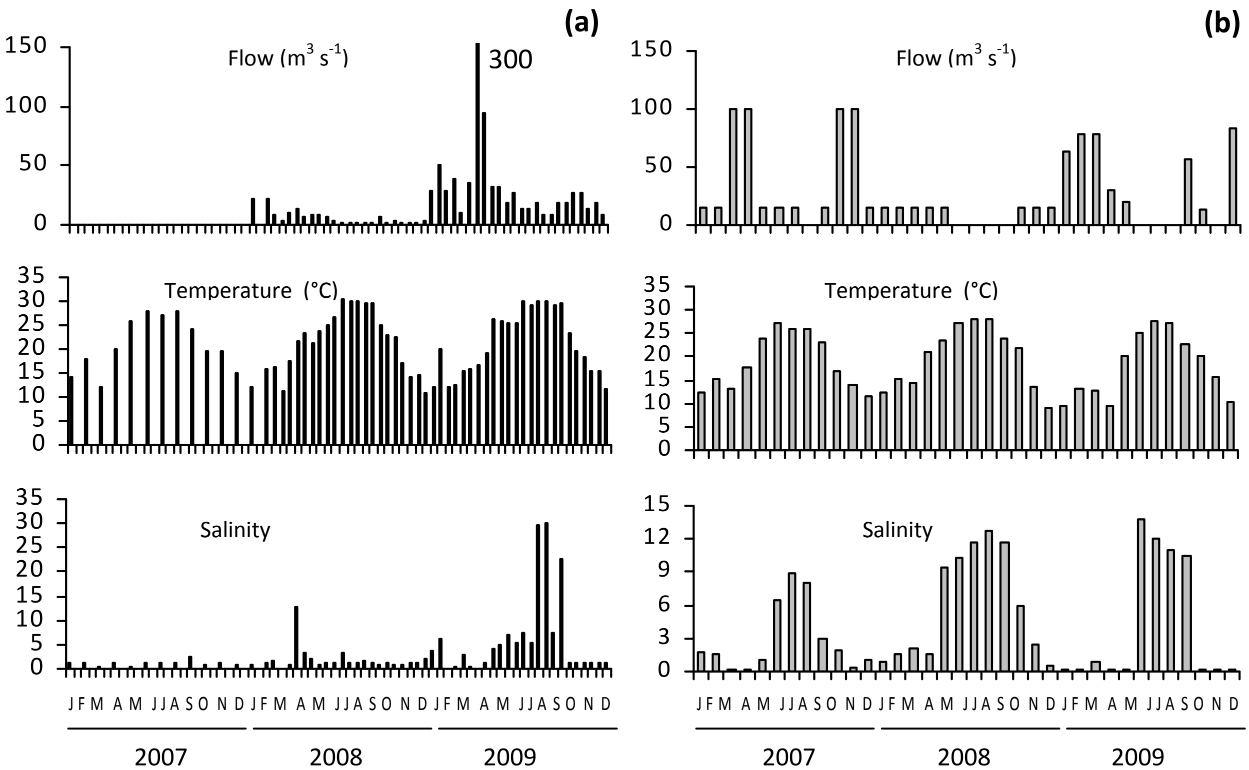

Figure 18: Seasonal variations of temperature, salinity and flow in the Seybouse estuary (a) and the Mafragh estuary (b), January 2007-December 2009.

In the outlets of the estuaries, the salinity is controlled by River inputs and to a lesser degree by tidal intrusion. In the wet period which extends approximately from November to April, continental inputs dominated the entire estuary, driving the salt wedge back towards the sea. Salinity values then decreased to between 0.5 and 1 pss (Figure 18a and b). During the dry periods in summer and autumn, marine intrusion dominated and increased the salinity over the entire estuarine layer. Therefore, the observed bottom salinities (not represented here) may be comparable to those of the adjacent shoreline, and the surface salinity ranged between 10 and 30 pss. In the spring and summer, the estuaries were marked by variable salinity depending on the tidal phase. During this period, the surface values fluctuated at some units, reflecting large marine intrusions (Figure 18a and b). During late summer and autumn, the marine connection of the Mafragh estuary was closed and it appeared to function as a non-tidal lagoon. There, the surface salinity increased to a maximum of 6 to 14 pss, depending on the historical freshwater inputs (Figure 18b).

1.2. Nutrient variability and fluxes at the estuaries' outlets

The waters from the mouth of the Seybouse were highly charged with dissolved nitrogen forms (DIN = NH_4 + NO_2 + NO_3) and PO_4, and the values were higher than any from the Mafragh estuary (Figure 19). The dominant character of the Seybouse was its high NH_4 levels which reached an average of 200 to 260 µM depending on the year; this represents more than 20 times the levels recorded in the outlet of the Mafragh. The oxidized forms of nitrogen, as NO_3 plus NO_2, always occurred in a low fraction compared to the NH_4, which represented more than 80 % of DIN. In contrast, in the Mafragh outlet, the oxidized form of nitrogen accounted for 60%. The Seybouse estuary also had high levels of PO_4, with an average value of 2.5 to 6 µM, and the maximum was recorded in the year 2007. Again, the PO_4 enrichment of the Seybouse waters relative to the Mafragh was several-fold (Figure 19a and b). The average level in the Mafragh ranged from 1 to 2.5 µM, and the maximum was found in the unusually wet year of 2009.

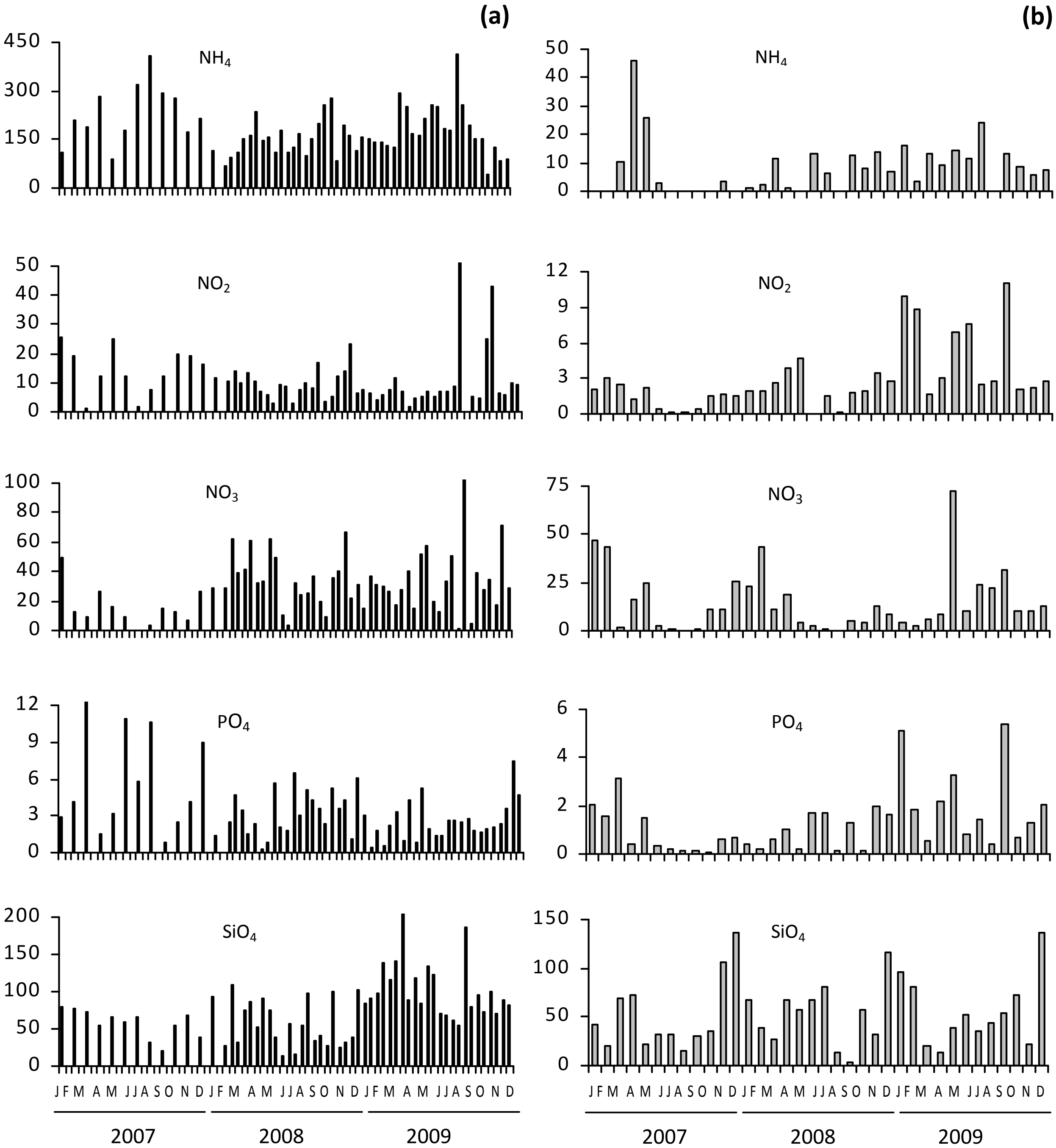

Figure 19: Seasonal variations of nutrient levels (µM) in the Seybouse estuary (a) and the Mafragh estuary (b), January 2007-December 2009.

The $Si(OH)_4$ levels, unlike those of DIN forms or PO_4, were low in both estuaries, particularly in the dry years of 2007 and 2008, when the average values decreased to 50 µM (Figure 19a and b). In the exceptionally rainy year of 2009, as seen in the figure 19, the $Si(OH)_4$ levels increased to 100 µM and 56 µM in the Seybouse and Mafragh outlets, respectively.

Because the estuaries buffer nutrient dynamics, the seasonal variations in the outlets were masked. Average levels in the wet period were slightly higher than those of the dry season, particularly in the Seybouse. However, the levels of NO_3 and $Si(OH)_4$ increase by 20 to 40% in the wet period compared to the dry ones. At the Seybouse outlet, NH_4 levels were always high, but paradoxically increased by 45% in the dry season. This trend may indicate that NH_4 is largely from urban inputs.

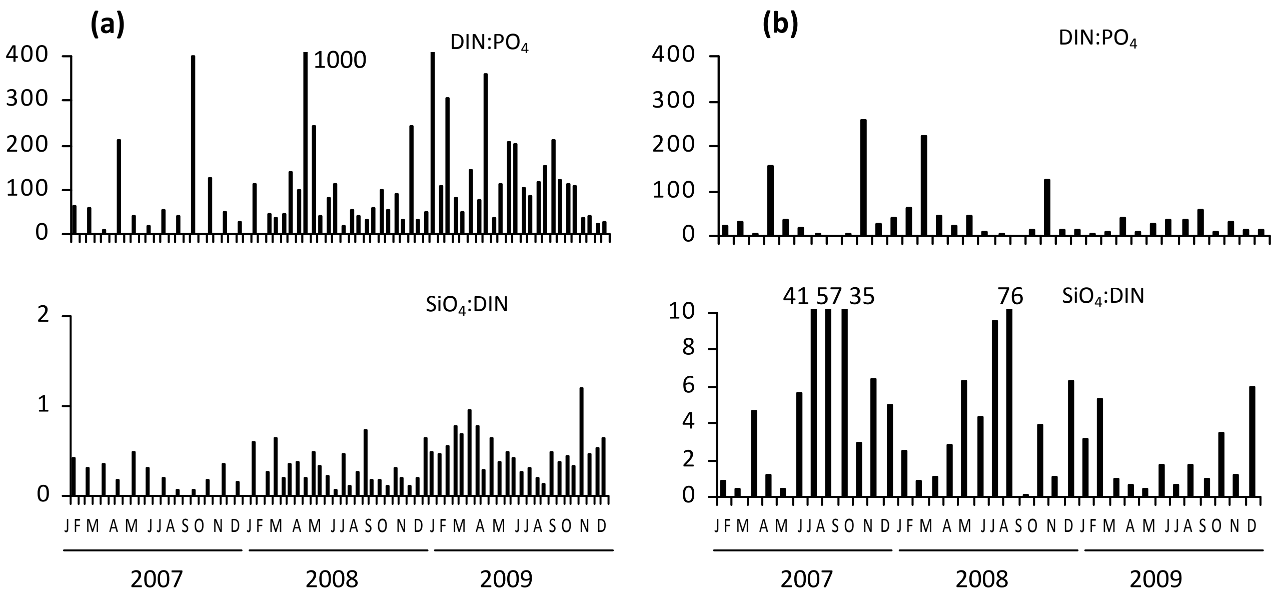

Figure 20: Variations in $DIN:PO_4$ and $SiO_4:DIN$ ratios in the Seybouse (a) and Mafragh (b) estuaries during the period January 2007-Décember 2009.

As shown in the figure 20a and b, the estuaries released waters with very imbalanced Redfield ratios ($DIN:PO_4$ and $Si(OH)_4:DIN$). The disturbance is clearer for the Seybouse estuary, where $DIN:PO_4$ reached an average of 92-135 and $Si(OH)_4:DIN$ did not pass 0.5 (Figure 20a). Not only did nitrogen inputs dominate in the mouth of Seybouse, but there was also a large decrease of $Si(OH)_4$ in the upper catchment, which was likely responsible for the sharp decrease in the $Si(OH)_4:DIN$ ratio or the increase of $DIN:PO_4$. Despite the relative high $DIN:PO_4$ ratio (20.8) in the Mafragh estuary, the $Si(OH)_4:DIN$ appears to be more balanced, its average varying between 2 and 13 (Figure 20b). For both estuaries, all of these ratios were more disturbed in the dry season, when $Si(OH)_4$ levels decreased as NID and PO4 increased.

Nutrient fluxes from the estuaries were highly variable between years, depending principally on River flow (Table 7). The Seybouse estuary introduced large amounts of all nutrients compared to the Mafragh estuary; it carried twice the oxidized nitrogen and Si-Si$(OH)_4$ and more than 20 times the N-NH_4. However, the two estuaries input comparable masses of P-PO_4. Only the Si-Si$(OH)_4$ fluxes were higher in the Mafragh estuary compared to the Seybouse, and only for the dry year of 2008. The Seybouse estuary delivered considerable fluxes of DIN in the heavy rainfall year of 2009, of which 84 % were in the form of N-NH_4. In contrast, the Mafragh estuary delivered less DIN, with a high fraction of oxidized forms as seen in the table 7.

Table 7: Nutrient fluxes (t yr^{-1}) and specific fluxes (t km^{-2} yr^{-1}; values between parentheses) delivered from Seybouse and Mafragh estuaries into the Bay of Annaba during the period January 2007 to December 2009. Calculated values of the Redfield molar ratios DIN:PO_4:SiO_4, annual yield precipitation and average annual flow are also given.

	Seybouse			Mafragh		
	2007	2008	2009	2007	2008	2009
Precipitation (mm)	650	418	936	730	528	820
Flow (m^3 s^{-1})	*	6	37	42	10	35
N-NH_4 (t yr^{-1})	*	371 (57)	3510 (543)	235 (73)	25 (8)	160 (50)
N-NO_2 (t yr^{-1})	*	26 (4)	117 (18)	31(10)	13 (4)	94 (29)
N-NO_3 (t yr^{-1})	*	102 (16)	512 (79)	228 (71)	70 (22)	207 (65)
NID (t yr^{-1})	*	500 (77)	4139 (640)	494 (154)	108 (34)	462 (144)
P-PO_4 (t yr^{-1})	*	15 (2)	100 (15)	42 (13)	8 (3)	91 (28)
Si-SiO_4 (t yr^{-1})	*	353 (55)	4865 (752)	2442 (763)	511 (160)	2259 (706)
DIN:PO_4	*	55	61	25	31	8
SiO_4:DIN	*	0.63	1.03	17.24	4.14	3.50

In addition, large amounts of Si-Si$(OH)_4$ were loaded from the estuaries in 2009 in their respective high flows. The maximum specific loading of DIN was on the order of 700 kg N km^{-2} y^{-1} in the Seybouse outlet and only approximately 150 kg N km^{-2} y^{-1} in the Mafragh. However, Si-Si$(OH)_4$ loading of the two watersheds was remarkably comparable in wet years (approximately 750 kg N km^{-2} y^{-1}) and within several tens kg N km^{-2} y^{-1} in dry years (Table 7). The P-PO_4 specific loadings were found important, ranging from 1 to 15 kg N km^{-2} y^{-1} according to the year. Most of these loadings occurred in winter coinciding with agricultural soil amendment. Because they were almost closed, the outlets delivered fewer nutrients in the rest of the year. In addition to the high masses introduced to the Bay via Seybouse, the loading ratios DIN:PO_4 and Si$(OH)_4$:DIN, were also unbalanced. The DIN:PO_4 ratio was above 30 and the Si$(OH)_4$:DIN was below 1.

1.3. The wet atmospheric deposition

Wet atmospheric deposition for NH_4 in the region of Annaba ranged from 0 to 54.4 µM during the period 16 October 2011- 22 May 2013 with an average of 13.6 µM. The maximum levels were observed in Autumn and Winter (Figure 21)

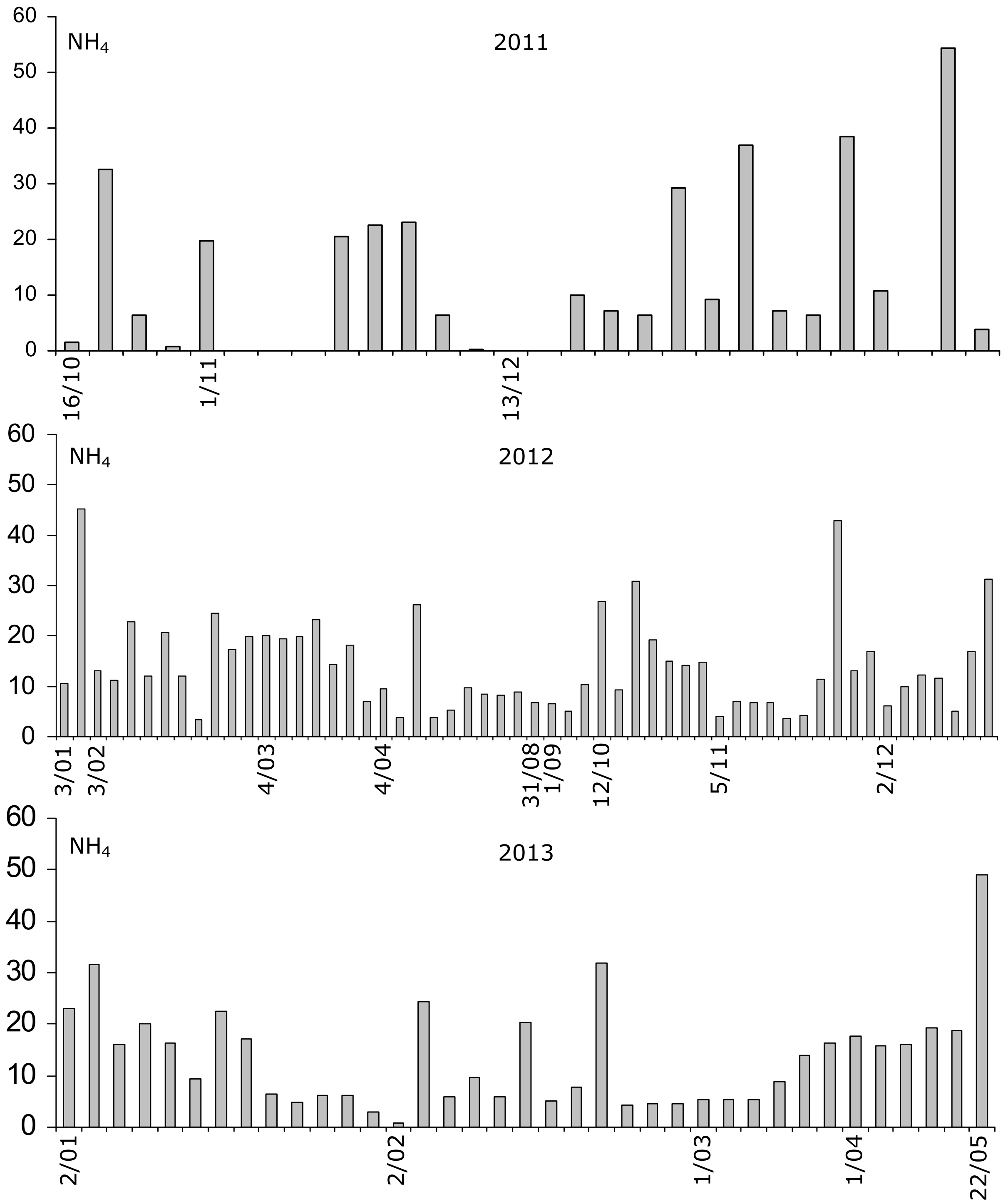

Figure 21: Variations on ammonium (NH_4) levels (µM) in wet atmospheric deposition for Annaba region during the period 16 October 2011-22 May 2013. Refer to Table 6 for non represented dates.

Concentrations of NO_3 in the study period also varied greatly, they were in the range of 0 and 74.7 µM (Figure 22) with an average of 10.76 µM. The figure 22 clearly shows that the year 2013 presented fewer concentrations than those of the years 2011 and 2012 (Figure 22).

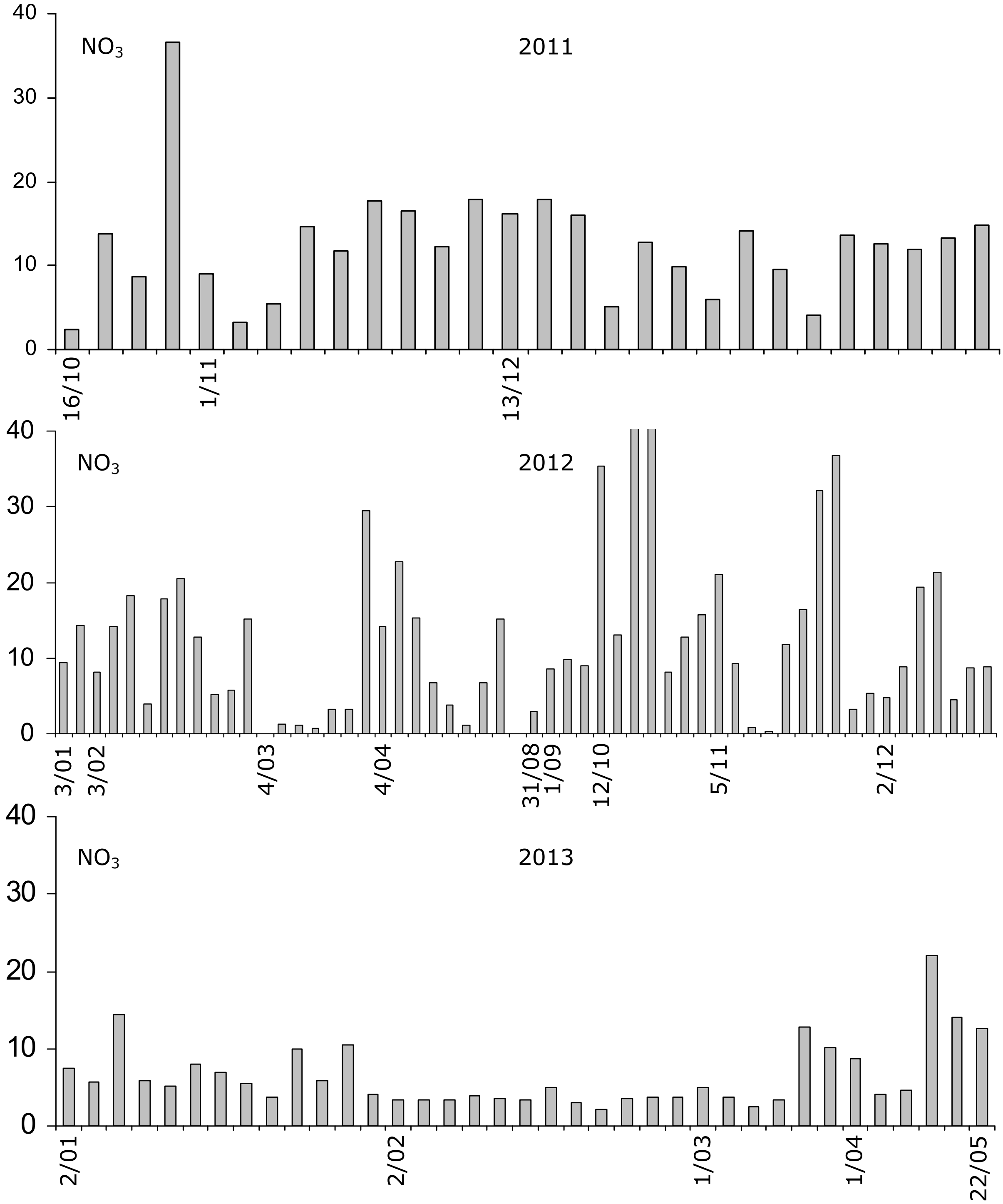

Figure 22: Variations on nitrate (NO_3) levels (µM) in wet atmospheric deposition for Annaba region during the period 16 October 2011- 22 May 2013. Refer to table 6 for non represented dates.

The minor fraction of DIN also changed considerably in the region of Annaba and ranged from 0 to 8.3 µM with an average of 1.5 µM (Figure 23). The highest concentrations were observed in Autumn 2012 (Figure 23).

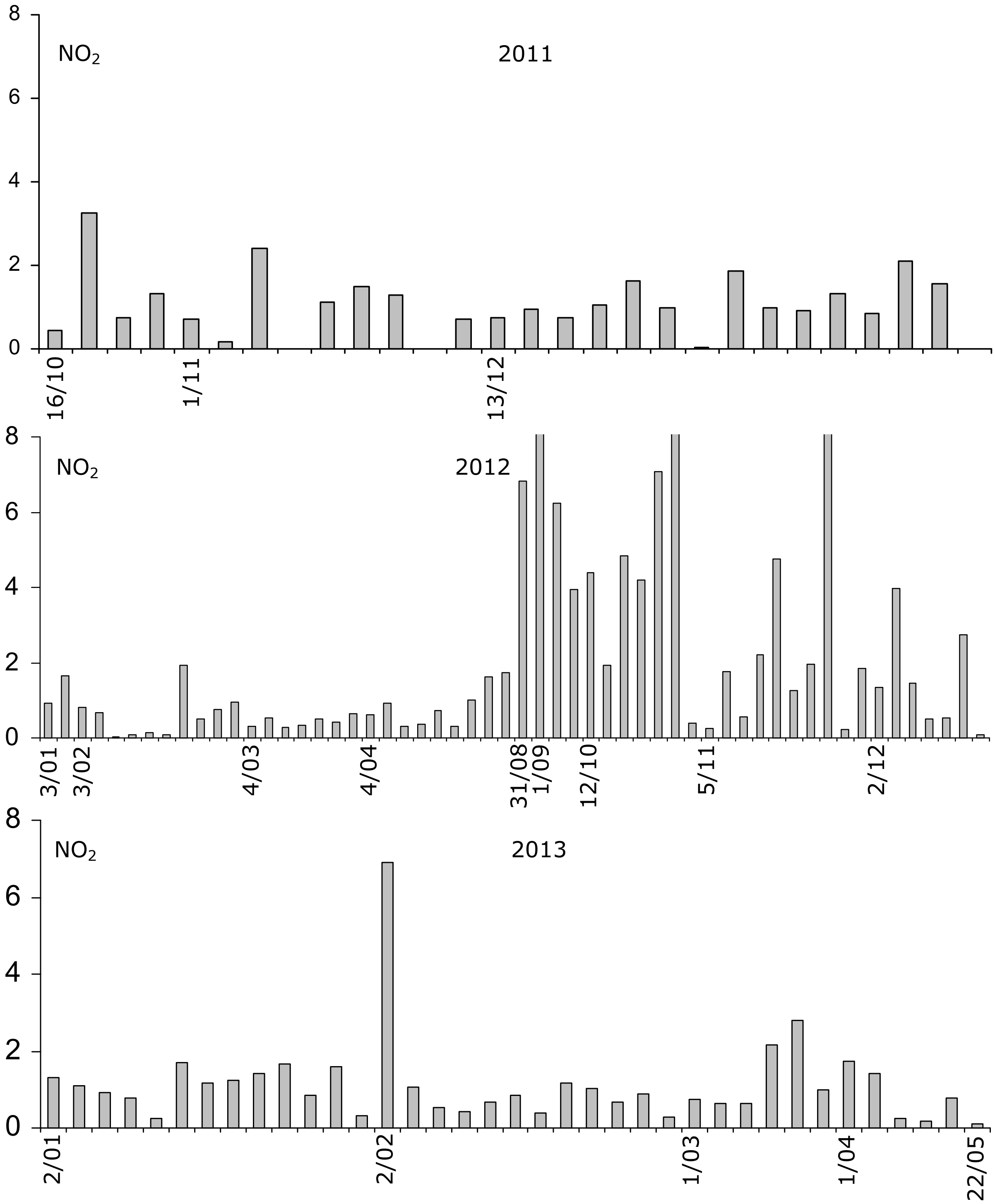

Figure 23: Variations on nitrite (NO_2) levels (µM) in wet atmospheric deposition for Annaba region during the period 16 October 2011- 22 May 2013. Refer to table 6 for non represented dates.

The DIN levels varied in the region of Annaba throughout the days and varied between 3.4 and 110.5 µM with an average in the study period of 25.8 µM (Figure 24). The highest levels were observed in Autumn (Figure 24).

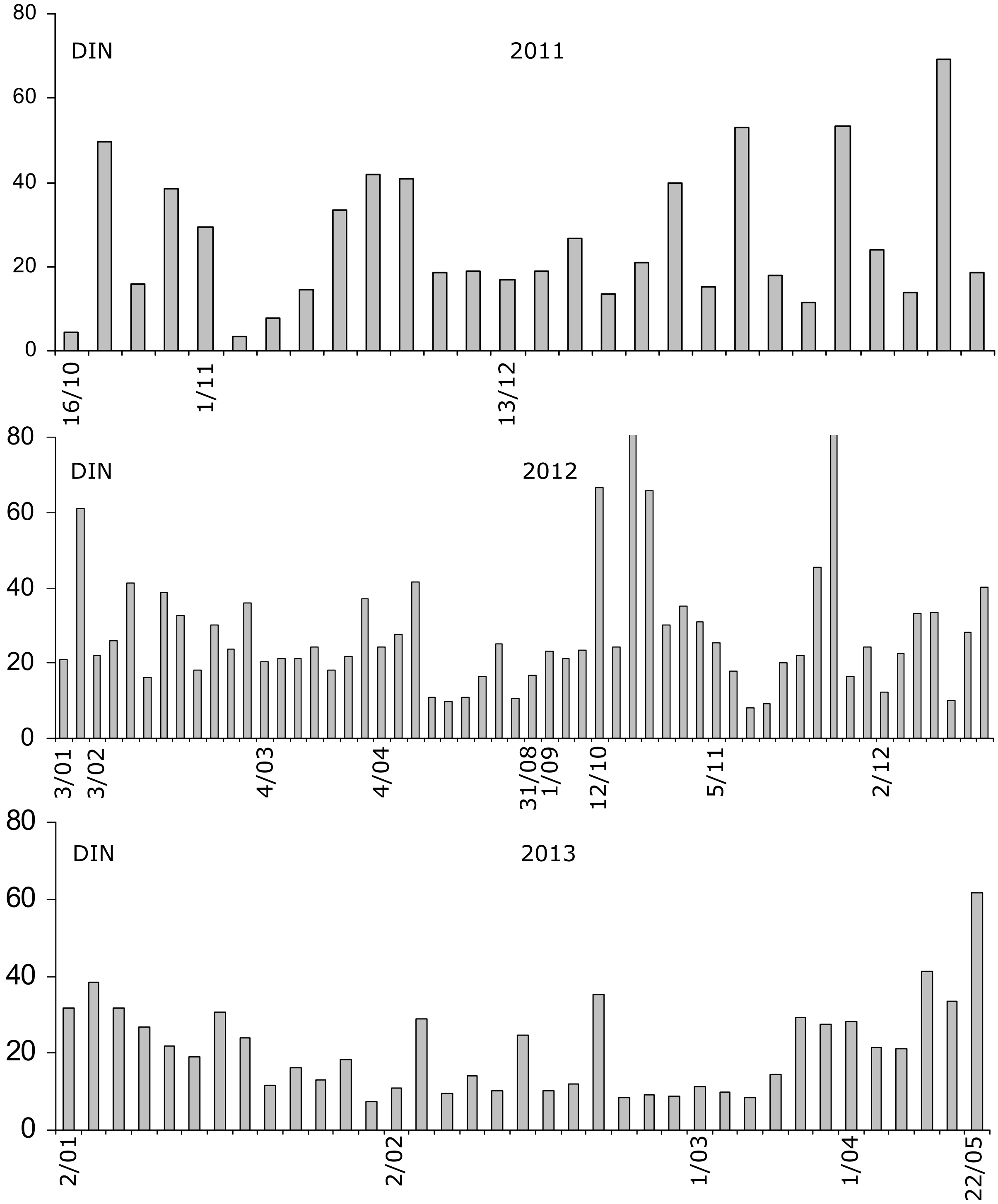

Figure 24: Variations on dissolved inorganic nitrogen (NID) levels (µM) in wet atmospheric deposition for Annaba region during the period 16 October 2011- 22 May 2013. Refer to table 6 for non represented dates.

As for DIN and its components, PO_4 concentration in the region of Annaba were highly varied and ranged from 0.05 to 4.45 µM with an average in the study period of 25.8 µM (Figure 25). Figure 25 clearly demonstrates that the highest levels were recorded in the Spring.

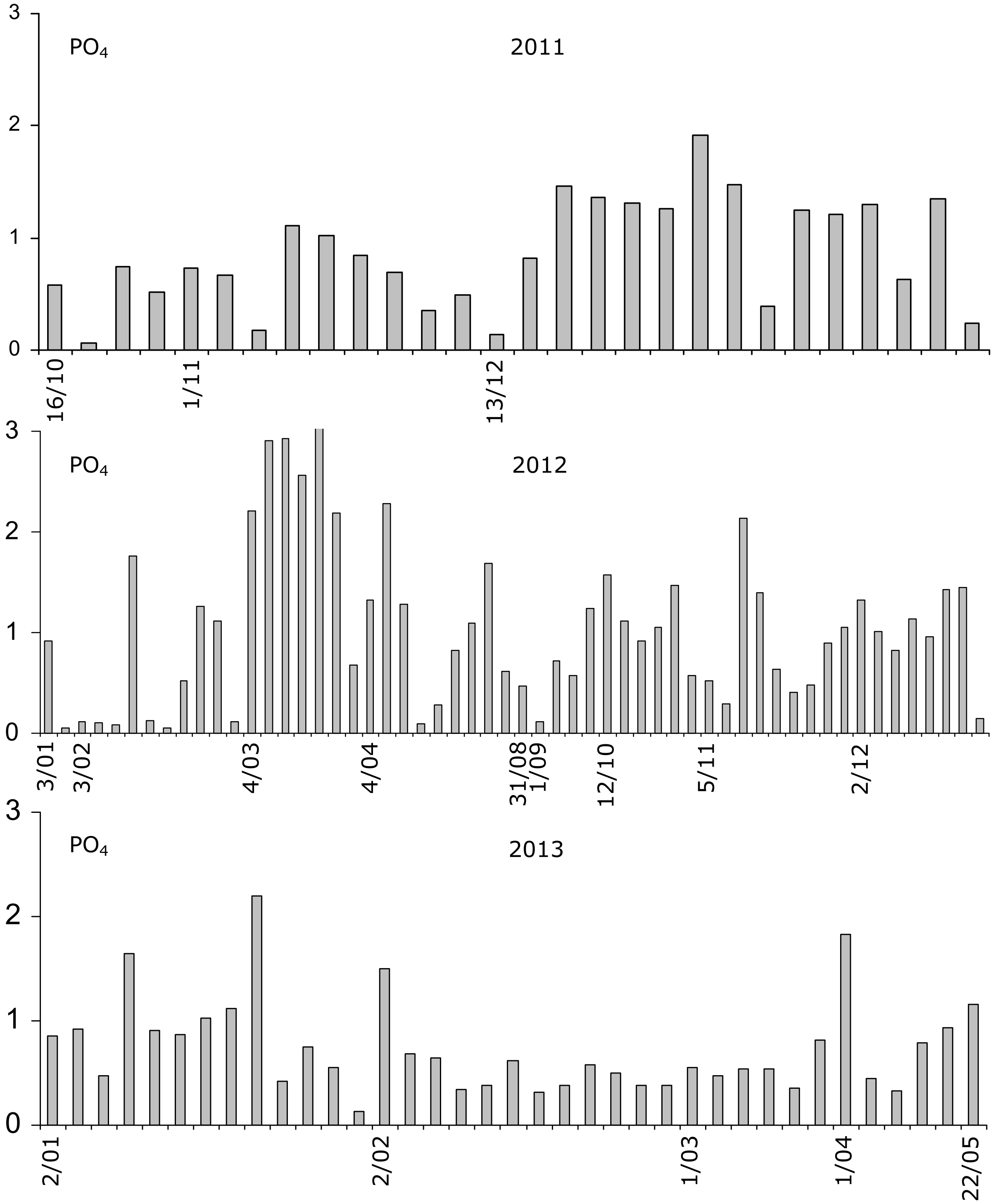

Figure 25: Variations on phosphate (PO_4) levels (µM) in wet atmospheric deposition for Annaba region during the period 16 October 2011- 22 May 2013. Refer to table 6 for non represented dates.

The $Si(OH)_4$ levels in the study period were ranged from 0.1 and 48.8 µM with an average of the study period of 25.8 µM (Figure 26). 2012 and 2013 presented clearly higher values compared with those of 2011. Like the PO_4 levels pattern, the highest concentrations were recorded in the Spring (Figure 26).

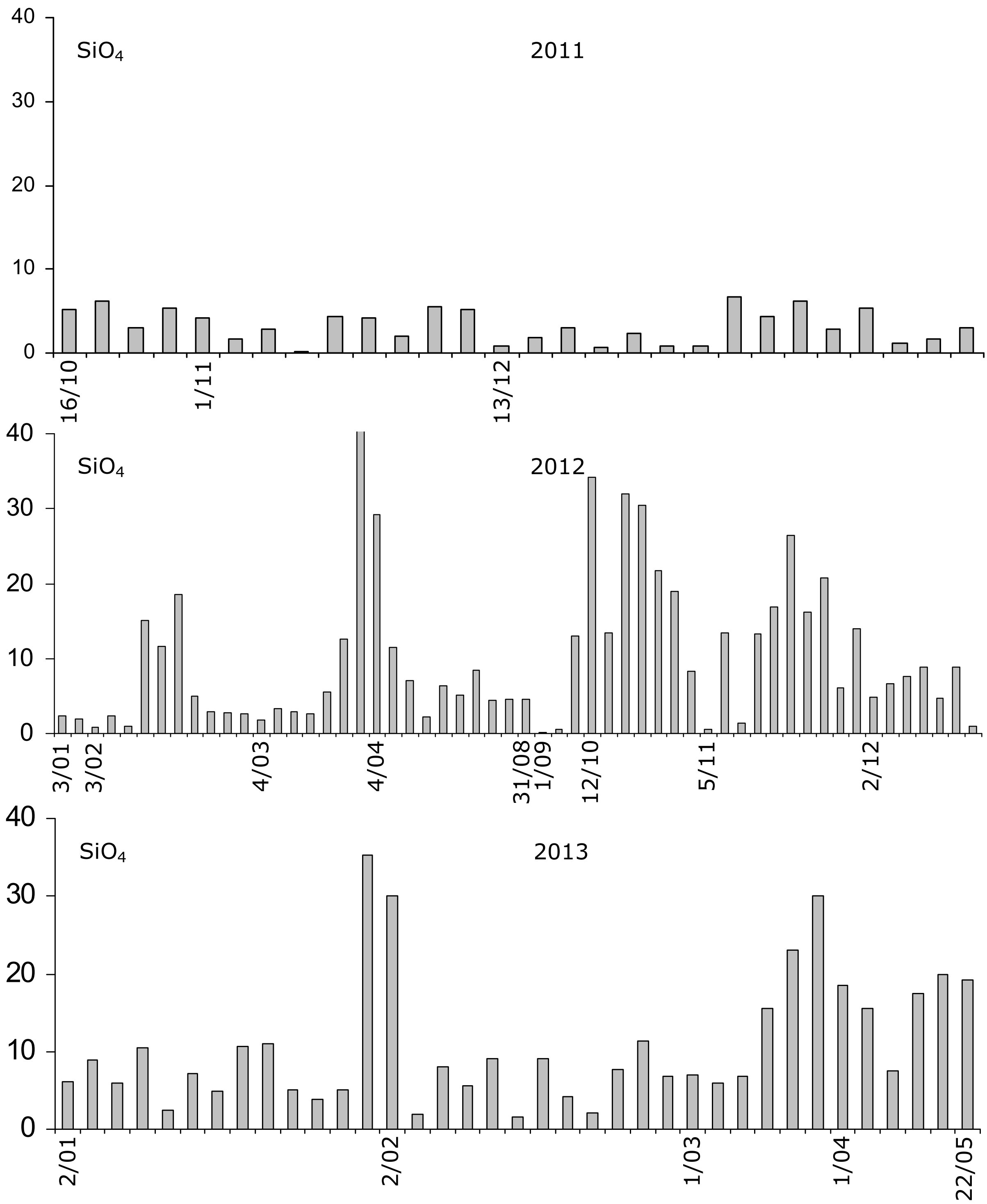

Figure 26: Variations on silicate (SiO_4) levels (µM) in wet atmospheric deposition for Annaba region during the period 16 October 2011- 22 May 2013. Refer to table 6 for non represented dates.

Seasonal mean of nutrient concentrations in wet atmospheric deposition during the period 16 October 2011 - 22 May 2013 in the region of Annaba are presented in the table 8.

Table 8: Seasonal mean of nutrient concentrations (µM) in wet atmospheric deposition during the period 16 October 2011 - 22 May 2013 in the region of Annaba. NID:PO_4 and SiO_4:DIN ratios are also given.

	NH_4	NO_3	NO_2	NID	PO_4	SiO_4	NID:PO_4	SiO_4:DIN
Autumn (D=33)	12,2	16,3	2,6	31,1	0,8	10,7	38,7	0,34
Winter (D=59)	14,1	9,1	1,1	24,3	0,8	6,2	29,9	0,26
Spring (D=28)	14,2	8,2	0,8	23,2	1,3	12,2	18	0,53
Summer (D=1)	6,8	3	6,8	16,6	0,5	4,6	35,6	0,28
2011-2013 (D=121)	**13,6**	**10,8**	**1,5**	**25,8**	**0,9**	**8,8**	**28,1**	**0,34**

Even if the daily variation of nutrient concentrations had not a clear tendency, seasonal mean concentrations followed a particular trend (Table 8). The reduced form of DIN was the dominant fraction of DIN (52.5 %) and it presented the highest mean in the Spring. In contrast, the DIN and its oxidized forms (NO_3 and NO_2) were higher in the Autumn (Table 8). The highest PO_4 mean concentration was in Spring while Autumn and Winter represented the same mean. As for PO_4, SiO_4 average was also high in Spring where it represented almost 1.5 times higher the total mean during the study period as it is shown in table 8. The Summer presented always the lowest mean concentrations (Table 8).

As shown in table 8, wet atmospheric deposition during the study period in the region of Annaba had imbalanced Redfield ratios (DIN:PO_4 and $Si(OH)_4$:DIN) within the seasons and they reached an average of 28.14 and 0.34 for DIN:PO_4 and $Si(OH)_4$:DIN respectively.

The DIN specific fluxes into the Bay of Annaba from the atmospheric wet depositions were not high, ranging from 260 to 279 kg km^{-2} y^{-1} depending on the year. The DIN average loadings for the three years investigated (January 2011-December 2013) was 267 kg $km^{-2}y^{-1}$ (Table 9). The PO_4 specific loadings in Annaba Bay were rather low, ranging from 18 to 20 kg km^{-2} y^{-1} with a mean annual flux of 19 kg $km^{-2}y^{-1}$. SiO_4 loadings found to be ranged from 148 to 206 kg $km^{-2}y^{-1}$ depending on the year with a mean of 180 kg km^{-2} y^{-1}. The loading ratios DIN:PO_4 and $Si(OH)_4$:DIN were 13.4 and 0.67 respectively (Table 9).

Table 9: Nutrient fluxes (F in t yr^{-1}) and specific fluxes (Fs in kg km^{-2} yr^{-1}) from wet atmospheric deposition in the region of Annaba during the period January 2011–December 2013. DIN:PO_4 and SiO_4:DIN are also given.

	2011		2012		2013	
	F	Fs	F	Fs	F	Fs
N-NH_4 (t/y)	50	124	49	124	57	142
N-NO_3 (t/y)	49	123	48	120	47	117
N-NO_2 (t/y)	6	15	7	17	8	19
NID (t/y)	104	261	104	260	111	279
P-PO_4 (t/y)	8	20	7	18	8	19
Si-SiO_4 (t/y)	59	148	74	184	83	206
DIN:PO_4	13	13	14.8	14.8	13.9	13.9
SiO_4:DIN	0.57	0.57	0.71	0.71	0.74	0.74

Chapter IV
Hydrology and nutrient variability in the Bay

Chapter IV: Hydrology and nutrient variability in the Bay

1. Hydrology in the Bay

The temperature ranged between 12°C and 28°C, with a minimum in February, a maximum in August and an average value of 19 to 21°C, depending on the station. Through the seasons and years, the surface salinity fluctuated between 23 and 37.9 pss (Figure 27). The lowest salinity values were recorded at the inner station B1, located at the Seybouse plume, and their averages varied in the range of 32 to 36.4 pss. The other inner station, B2 of the Mafragh plume, showed comparable but elevated surface values ranging from 34 to 36.8 pss (Figure 27b).

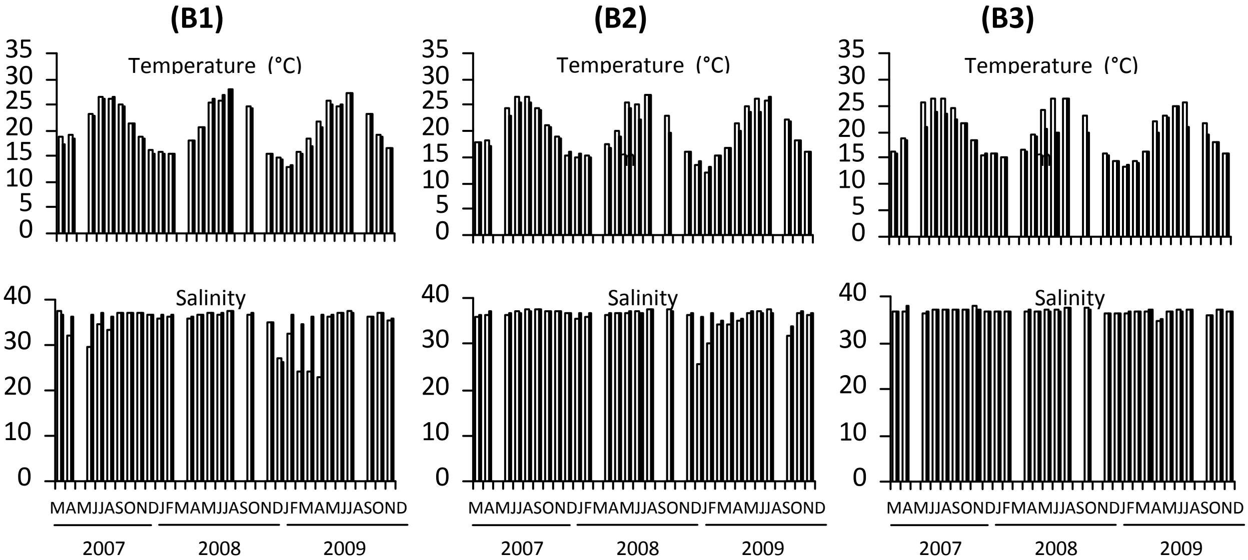

Figure 27: Seasonal variations of temperature and salinity in the three stations of the Bay of Annaba, March 2007-December 2009. □ Surface values ■ Bottom values.

Surface salinity values increased to 36.5 to 37 pss in the outer coastal waters (station B3) but remain stable throughout the seasons. Here, freshwater influences were so limited that the salinity deviation did not exceed 0.5 pss (Figure 27c), a value that reflects the major hydrological features of the Modified Atlantic Water (MAW) that prevails the Bay of Annaba. The estuarine influence on coastal waters was also expressed by the stratification in the shallower waters of station B1 and to a lesser extent in station B2. These influences did not reach the outer waters of station B3 because of thorough mixing and a constant salinity through the entire water layer (Figure 27c). Instead, this area is under the influence of external waters via the residual current of MAW penetrating the Bay.

2. Nutrient variability in the Bay

Station B1 directly reflected to the Seybouse inputs and showed the highest levels in all nutrients, as shown in figure 28a. Through the years the DIN surface levels remain almost unchanged, fluctuating around 10 µM in the Seybouse plume, and NH_4 is the main fraction of DIN. Only the rainy year of 2009 showed significantly elevated values (Figure 28a).

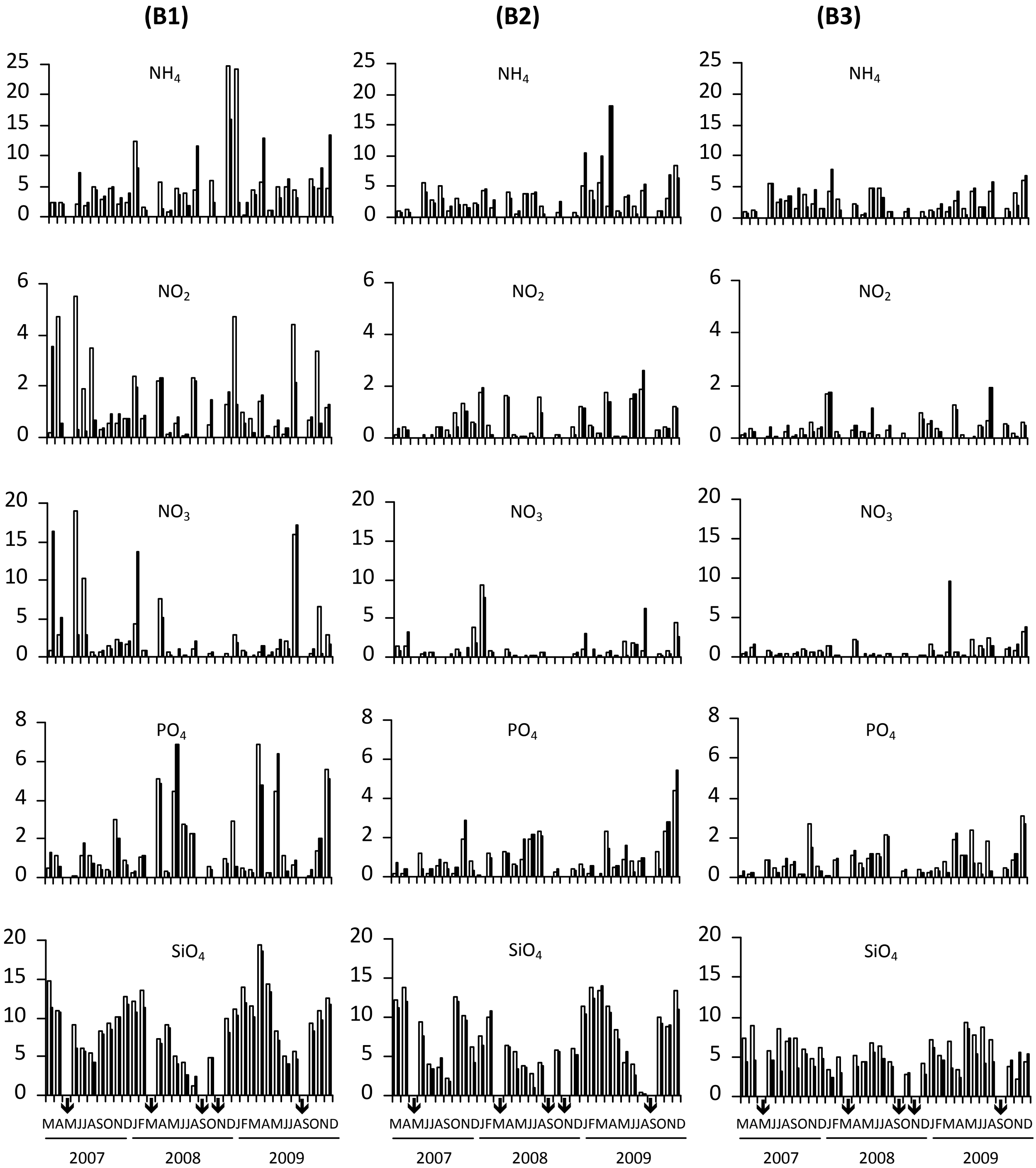

Figure 28: Seasonal variations of nutrient levels (µM) in the three stations of the Bay of Annaba, March 2007-December 2009. ☐ Surface values ■ Bottom values.

Station B2 corresponds to the Mafragh plume, and the DIN levels were half those of station B1, with the NH_4 proportion still forming the essential part of DIN. Station B3 had the least DIN, which reflects the characteristics of external waters. The NH_4 fraction was the dominant form within DIN of surface waters (Figure 28c).

Large amounts in DIN appeared in winter after the continental inputs (Figure 28). At times the DIN levels were lower, especially in the surface waters at station B3, but in no season were they depleted. Even if NO_3 ions are known to originate from River discharges, their levels in the Bay throughout the year are only in the order of 1 µM in station B2 and B3 and 3 µM in the Seybouse plume (B1). Dilution effects undoubtedly lowered the levels of this nutrient because its level in the Seybouse inputs was about 30 µM. Because of the high hydrodynamic forcing that induces thorough mixing in winter and spring, the water column in the shallower waters of station B1 showed the same DIN levels. The other deeper stations showed relatively high values at the bottom compared to the surface (Figure 28b, c).

The average surface levels of PO_4 for the whole area varied from 1 to 1.7 µM, and Seybouse plume station always had the highest value (Figure 28). The maximum levels rose in the wet period because of continental discharge, and reached 4 µM and 2 µM in the Seybouse and Mafragh plume, respectively. Station B3 which is weakly influenced by continental discharges, had the lowest average values (Figure 28c) throughout the year (0.7 to 1.2 µM), but high levels could be recorded in winter when River discharge can reach further into the Bay (Figure 28c). As for DIN, the levels of PO_4 at the bottom were comparable to surface values because of winter hydrodynamic mixing. There were however, some perceptible differences between the Mafragh plume and the outer station (Figure 28b, c).

Similar to the DIN levels, $Si(OH)_4$ at the surface followed a clear spatial distribution with large differences between the station plumes and the outer station (Figure 28). In the plumes of the estuaries, average surface levels were on the order of 6 µM for the Seybouse and 4 µM for the Mafragh. On the surface of the outer waters at station B3, $Si(OH)_4$ increased to 2 µM but fluctuated greatly throughout the years, between 1 and 9 µM (Figure 28c). The bottom levels were always comparable in the plume stations, but were significantly different from the deeper station in the outer waters.

The Redfield ratios were generally disturbed in all stations in both the surface and bottom waters (Figure 29). Depending on the station and the year, the DIN:PO4 ratios were below 10 in 50 to 70 % of samples and the Si(OH)4:DIN ratios were below 1 in 50 to 70 % of samples (Figure 29). In all stations, the DIN:PO4 average ratios varied between 2.3 and 11.6, except at the station B1 in 2007 which recorded a ratio of 30. Even though the average values of the Si(OH)4:DIN ratios fluctuated around 1 (0.86 to 1.6) in all of the stations, they were also imbalanced and below 1 for 50 to 70% of samples (Figure 29).

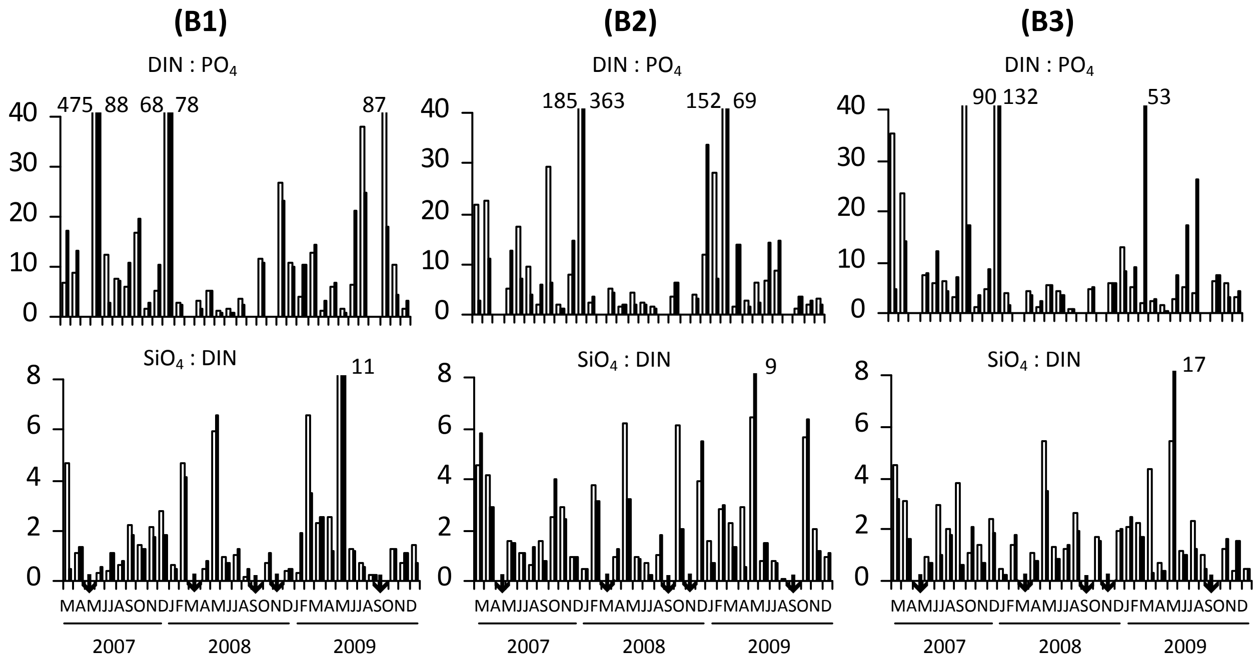

Figure 29: Variations of DIN:PO_4 and SiO_4:DIN ratios in the Bay of Annaba during the period March 2007-December 2009. ☐ Surface values ■ Bottom values.

General Discussion

General discussion

The objective of this work was to estimate the inorganic nutrient (N, P and Si) fluxes from Seybouse and Mafragh estuaries and from the wet atmospheric deposition and to evaluate how much the transfer influenced the distribution of nutrient levels in the Bay of Annaba. Very little is known about the hydrology and chemistry of the Algerian estuaries and their adjacent coasts. Though there is some information about the seasonal nutrient (DIN and PO4) inputs from the Mafragh estuary (Khélifi et al., 2006) and the works of Ounissi and Fréhi (1999) and Fréhi et al. (2007) describe the DIN and PO_4 observed in the inner part of the Bay of Annaba, information on the Bay hydrology is still lacking.

1. The estuaries

The two estuaries introduced large amounts of inorganic nutrients into the Annaba Bay: DIN: 2,675; P-PO_4 t yr^{-1}: 105 t yr^{-1} and Si-$Si(OH)_4$: 4,347 t yr^{-1}. The Seybouse alone contributed over 80% in of the DIN. For $Si(OH)_4$, the two estuaries supplied comparable fluxes, which originated from land weathering. According to this study, the Seybouse appears to be the major anthropogenic source influencing the chemistry of the Bay of Annaba. In the plume of Seybouse, Fréhi et al. (2007) and Ounissi and Fréhi (1999) reported very high values in NH_4 (24-40 µM) and PO_4 (2-17 µM). The Seybouse waters were heavily charged with NH_4 throughout the year, with an average as high as 200 µM. The Seybouse waters were strongly dominated by the NH_4 form of reduced nitrogen (80%), which is unusual, compared to the major Mediterranean Rivers where NO_3 dominates. For Mediterranean Rivers, the EEA (2007) reports elevated values of NO_3 ranging from 20 to 376 µM, and in the Ebro River, NH_4 did not exceed 7% of the DIN forms (155 µM) according to Ibáñez et al. (2008). These contrasts may be related to the untreated household wastewaters that are released into the Seybouse River-estuary. Additionally, the high PO_4 levels (4 µM) characterizing the River suggest a strong influence of domestic wastewater. The implementation of European water quality legislation has had a direct impact on the Mediterranean coastal areas. PO_4 levels decreased 6-fold between the late 1980s and 2002 (Torrecilla et al., 2005) for the Ebro River. In addition, the Po River (Cozzi and Giani, 2011), the Rhone River (Diaz et al., 2008), the Tèt River (Garcia-Esteves et al., 2007), the Gediz River (Suzal et al., 2008) and several

Greek Rivers such as the Pinios (Bellos et al., 2004) and Axios River (Nikolaidis et al., 2009) all saw significant reductions in nutrient loads.

By contrast to the Seybouse estuary, the Mafragh estuary had low levels of all nutrients, and within the nitrogen pool, the NH_4 fraction represented only 30%. However both estuaries seem to be impoverished in $Si(OH)_4$ owing to the estuarine buffering (Canton et al., 2012; Hallas and Huettel, 2013) and to the reservoirs retention (Avilés and Niell, 2007; Humborg et al., 2006; Meybeck and Vörösmarty, 2005) in the upper catchments. Before reaching the coast, riverine nutrients passes through estuaries which act as filters for material derived from land (Canton et al., 2012; Hallas and Huettel, 2013). The disturbance in the quality of water entering the Bay was also expressed in unbalanced Redfield molar ratios. The $Si(OH)_4$:DIN molar ratio for Seybouse waters was low in all seasons, and fluctuated depending on the year from 0.25 to 0.5. In contrast, the Mafragh waters had elevated $Si(OH)_4$:DIN ratios, ranging on average from 2.2 to 13.4. The lesser amount of $Si(OH)_4$ in the Seybouse discharge (73 µM in average) along with the high DIN levels led to the low Si(OH)4:DIN ratio. Even though SiO_4 was also low in the Mafragh estuary, the $Si(OH)_4$:DIN ratio was unbalanced because the anthropogenic inputs was also low. In this case, the Mafragh estuary may be a good example of $Si(OH)_4$:DIN molar ratio trends being controlled by human nitrogen inputs rather than retention in estuaries or reservoirs. Controlling the nitrogen inputs in the catchments therefore seems to be a higher priority than trying to increase Si by lessening dam construction, in particular for Mediterranean sub-arid regions. As opposed to DIN and PO_4 levels, Si(OH)4 decreases significantly in most Mediterranean (Billen and Garnier, 2007; Ludwig et al., 2009; Ounissi and Bouchareb, 2013) and European Rivers (Conley, 2002; Humborg et al., 2000) owing to the reduction of River discharge and to the retention of dissolved and biogenic silica retention by dams (Conley et al., 2000). Additionally, the Si(OH)4:DIN was always below the phytoplankton requirements in Seybouse waters and about 30% of samples from the Mafragh outlet. Not only did the $Si(OH)_4$ decrease, but the levels of DIN increased under large anthropogenic inputs from the lower Seybouse catchment. The high and balanced $Si(OH)_4$:DIN values in the Mafragh may be related to its large marshland water supply, despite some human population and activity over the catchment. In addition, the

NID:PO4 molar ratio was also unbalanced in all of the Seybouse samples, with average values varying in the range of 90-135 according to the year. The excess of DIN compared to PO_4 seems to indicate an influence of agricultural waste rather than domestic point source inputs. On the other hand, the much higher level of NH_4 compared to NO_3 rather suggests that domestic wastes do impact this estuarine environment. In the Mafragh outlet, the DIN:PO_4 molar ratios were below the phytoplankton needs about half the time, and the annual average values ranged from 24 to 50. Because of the dominance of NO_3 jointly and low levels of PO_4, the Mafragh waters are most likely influenced most by agricultural fertilizers.

The DIN specific loadings from the Seybouse outlet were high, ranging from 77 to 640 kg N km^{-2} y^{-1} depending on the year. These amounts may be considered among the highest in Mediterranean Rivers (EEA, 2007; Ludwig et al., 2009; Ounissi and Bouchareb, 2013). In contrast to Mafragh outlet where DIN specific loadings were rather low (34 to 154 kg N km^{-2} y^{-1} in average), Nitrogen comes from both diffuse and urban sources, the former being often dominant in agricultural basins (Billen and Garnier, 1999; Sebilo et al., 2003). P-PO_4 specific loadings were elevated (3 to 28 kg P km^{-2} y^{-1} in average). These masses may also be considered elevated compared to Mediterranean Rivers (EEA, 1999; Ludwig et al., 2009). Phosphorus, by contrast, is massively brought into River water through urban wastewater discharge, so that point sources of P are dominant over diffuse sources linked to soil erosion and leaching in most populated River basins (Billen and Garnier, 2007). Even though levels of PO_4 were important in Seybouse outlet waters, the specific loadings in the catchment were paradoxically low (2 to 15 kg P km^{-2} yr^{-1}). The low loadings in DIN of Mafragh estuary compared to Seybouse one, is not only because of the smaller human population in the watershed, but may also be linked to the buffering effect of the Mafragh marshland, which provides nutrient sinks. The loadings of Si-Si$(OH)_4$ were remarkably comparable between the two estuaries in both wet and dry years (in wet years (≈750 kg/km²/y) and several tens kg/km²/y in dry years (Table 7)). The major portion of these loadings took place in winter leachings coinciding with agricultural soil amendment. In the wet seasons, the River outlets deliveries of nutrients were almost no when the exchanges between the River and the sea were in their minimum.

In addition to the heavy nutrient loads introduced into the Bay, especially via Seybouse, the loading ratios of DIN:PO_4 (> 30) and Si$(OH)_4$:DIN (<1), were also unbalanced, suggesting that P and Si may be the limiting factors for coastal phytoplankton growth. Intensification of agricultural practices and the recent reduction of phosphates in washing powders have contributed to increase greatly the N:P ratios. Therefore, coastal marine phytoplankton production would be mainly controlled by P, which is the limiting nutrient at the River mouths (Ounissi and Bouchareb, 2013).

2. Wet atmospheric deposition

The mean concentrations of DIN and its components from the atmospheric deposition in the region of Annaba were among the lowest levels in the Mediterranean region. DIN, NH_4, NO_3 were 3-4 folds less than those in Erdemli, Turkey (Koçak et al., 2010). The minor fraction of DIN (NO_2) was also 2 times lower while PO_4 mean concentrations were comparable in both places (Table 10). On the contrary, only the average concentration of Si was more than 4 times higher in the Bay of Annaba than in Erdemli, Turkey as it is indicated in table 10.

Table 10: Wet atmospheric deposition concentrations (µM) in Annaba region during the period January 2011 to December 2013 and comparison to other Mediterranean regions. DIN:PO_4 and SiO_4:DIN are also given.

	NH_4	NO_3	NO_2	DIN	PO_4	SiO_4	DIN:PO_4	SiO_4:DIN	Reference
Annaba, Algeria 2011-2013	13,6	10,8	1,5	25,8	0,9	8,8	28	0,34	This study
Erdemli, Turkey 1999-2007	46	44	3	93	0,7	1,9	133	0,02	Koçak et al., 2010
Heraklion, Crete, Greece Sep1999–Sep 2000	21	18	-	39	0.1	-	390	-	Markaki et al., 2003
Tel Shikmona (Haifa) Palestine Jan1992–Mar1998	25	41	-	66	0.6	-	110	-	Herut et al., 1999
Ashdod, Palestine Nov1995–Mar 1998	45	57	-	102	0.6	-	170	-	Herut et al., 1999

Also, the mean concentration of DIN in Annaba region was 1.5, 2.5 and 4 times lower than Heraklion Crete, Greece (Markaki et al., 2003), Tel Shikmona, Palestine (Herut et al., 1999) and Ashdod, Palestine (Herut et al., 1999) respectively (Table 10). In contrast, PO_4 mean concentrations in Annaba region were 1.5 folds higher than those of Palestine stations (Tel Shikmona and Ashdod) while they were almost 10 times higher compared with rainwater concentrations in Greece (Heraklion Crete). Thus, the abundance of DIN and scarcity of SiO_4 and

PO_4 rain concentrations in these Mediterranean regions conducted to very disturbed ratios of DIN:PO_4 and SiO_4:DIN (Table 10). DIN:PO_4 and SiO_4:DIN ratios were being 28 and 0.34 respectively and were somewhat balanced compared to the disturbed ones (133 and 0.02) calculated by Koçak et al. (2010) as it can be seen in table 10. Mainly inorganic nitrogen and its components in the region of Annaba were found lower than those calculated in other regions in the northern and eastern Mediterranean basin (Table 10) may be because the former is less exposed to the aerosol or anthropogenic pollution. The abundance of DIN in Turkey (Erdemli station) and Greece (Heraklion Crete) can be related to aerosol transported from Europe (Dulac et al., 1987; Bergametti et al., 1989; Gullu et al., 1998); Also, the elevated DIN concentrations in Tel Shikmona and Ashdod (Palestine) may be the effect of the eolian dust transported from Middle Eastern and Arabian Deserts (Guerzoni et al., 1999; Kubilay and Saydam, 1995).

Several studies have been interested to assess the flux of atmospheric depositions (Ganor and Mamane, 1982; Ganor et al., 1998; Chester et al., 1993; Guerzoni et al., 1999) but almost all of them focused their investigations on a large scale (Koçak et al., 2010 for the Northeastern Levantin Bassin (11000 km^2), Violaki et al., 2010 in the Eastern Mediterranean (170 10^6 km^2) and Markaki et al., 2008 for all the Mediterranean basin (250 10^6 km^2). Because of the small area of the Bay of Annaba (400 km^2), it would be unwise to compare our results to the data from the whole Mediterranean. However, the comparison may be useful for equal areas, as expressed by the specific loading (kg/km^2/y).

Table 11 shows the mean nutrient fluxes and discharges from studied Rivers and wet atmospheric deposition. Annual mean water discharge for Seybouse and Mafragh were found to be 21.5 and 29 m^3 s^{-1}, respectively. Discharges of Rivers show similar pattern of precipitation with highest values during rainy years. Table 11 clearly indicates that Mafragh is a typical example for the least polluted Rivers with low NH_4, DIN and PO_4, but a high SiO_4 fluxes compared with those of Seybouse. On the other hand, fluxes of NH_4, DIN and PO4 for Seybouse River imply that this fresh water source is substantially influenced by agricultural activities. It should also be noted that the Bay of Annaba received directly significant urban wastes from Boujemaa effluent (205 and 155 t y^{-1} for DIN and PO_4 respectively) and industrial wastes from FRTIAL sewer (950 and 163 t y^{-1} for DIN and PO_4 respectively) as demonstrated in table 11.

Table 11: Comparison between nutrient fluxes (t yr^{-1}) from Rivers (2007-2009), wet atmospheric deposition (2011-2013) and urban waste and industrial wastes (2006) delivered into the Bay of Annaba and percentages of each source of loading (%; values between parentheses). The Redfield molar ratios DIN:PO_4:SiO_4, estimation of total inputs to the Bay, annual yield precipitation and average annual flow are also given

	Urban waste (Boudjemaa)	industrial waste (FERTIAL)	Seybouse River	Mafragh River	Continental inputs (Rivers)	Atmospheric wet deposition	Total inputs to the Bay
Precipitation (mm)	0.16	0.87	668	693	163	620	
Flow (m^3 s^-)	2	11	21.5	29	50,5	*	*
N-NH_4 (t yr^{-1})	159 (5)	801 (26)	1941	140	2081 (68)	52 (1)	3073
N-NO_2 (t yr^{-1})	18 (11)	20 (12)	72	46	118 (72)	7 (4)	163
N-NO_3 (t yr^{-1})	28 (4)	128 (19)	307	168	475 (70)	48 (7)	679
NID (t yr^{-1})	205 (5)	950 (24)	2320	355	2675 (68)	107 (3)	3937
P-PO_4 (t yr^{-1})	155 (36)	163 (38)	58	47	105 (24)	8 (2)	431
Si-Si$(OH)_4$ (t yr^{-1})	*	*	2609	1737	4346 (98)	72 (2)	4418
DIN:PO_4	1.3	5.8	58	21	25.5	13.4	9
SiO_4:DIN	*	*	0.83	8,29	1.6	0.67	1.12

Inorganic nitrogen species (DIN = NO_2 + NO_3 + NH_4) fluxes to the Bay of Annaba were dominated by the riverine pathway with a mean contribution being more than 68% for DIN. Riverine phosphate flux (24%) was more than 17 times higher in rain water and it had a substantial contribution to the phosphate pool in the Bay of Annaba. SiO_4 inputs were almost exclusively dominated by riverine fluxes (98%) and only 2% of the Si was attributed to atmospheric source. The atmosphere was found to be a low source of nutrients to the surface waters in such reduced surface scale as the Bay of Annaba (400 km^2) with a mean contribution of 3, 2 and 2% for DIN, PO_4 and SiO_4 respectively. Atmospheric molar ratios were found to be 28 and 0.34 for DIN:PO_4 and SiO_4:DIN respectively. These ratios suggested that atmospheric source has a weak effect on the chemistry of the waters of the Annaba Bay.

The Bay

The disturbed estuarine inputs have strong effects on impact the adjacent coastal water. The estuary plumes of Seybouse and Mafragh always show high levels compared to the outer waters, where nutrient levels declined 3-fold for DIN and Si$(OH)_4$ and by 2-fold for PO_4. The Seybouse plume was highly enriched by NH_4 (2.8 to 7 µM) and by PO_4 (1 to 2.2 µM) throughout the seasons, depending on estuarine inputs. These spatial distributions have also been reported by Fréhi et al. (2007) and Ounissi and Fréhi (1999).

It is noteworthy that the Bay of Annaba has average depth of 60m; perimeter of about 100 km and an area of 400 km^2. It is the unique Bay in Algeria that receives discharges from two important rivers (Seybouse and Mafragh) which drain together a surface of about 9700 km^2.

Table 12: Drainage basins Characteristics of the Bay of Annaba and comparison with the Mediterranean and black sea

	Land area (10^3 km^2)	Sea area (10^3 km^2)	Land/sea ratio	References
Mediterranean	5526	2508	2.2	Ludwig et al., 2009
Black Sea	2398	460	5.2	Ludwig et al., 2009
Annaba Bay	**9.7**	**0.4**	**24**	This study

The average land to sea area ratio is 24 (Table 12). This, contrasts strongly with the Mediterranean and the Black Sea, it is almost 11 and 5 times greater than the Mediterranean and the Black Sea respectively as it is shown in table 12. The inputs from land play a greater role in the Bay of Annaba, because the perimeter to surface ratio of the basin is particularly high. All these peculiar and contrasting characteristics should likely be reflected in the water nutrients concentration and the ecosystem structure and dynamics.

Compared to the Bay of Annaba, the Bay of Algiers (Samson-Kechacha, 1981; Bachari Houma, 2009) is less enriched with all nutrients, where NO_3, $Si(OH)_4$ and PO_4 varied respectively in the range of 0.1 to 5 µM, 0.1 to 5 µM and 0.05 to 0.8 µM. At other similar Mediterranean coastal waters, for example the Bay of Tunis, Tunisia (Daly Yahia-Kafi et al., 2005); the Bay of Izmir, Turkey (Kucuksezgin et al., 2006), the Bay of Strymonikos, Greece (Sylaios et al., 2006), the Catalan coastal inner waters, Spain (Flo et al., 2011), the Bay of Annaba show comparable spatial and temporal tendencies of nutrient concentrations. The inner Bays directly submitted to continental discharge, are always markedly enriched. However, the outer waters showed different enrichment according to local hydrological conditions. Besides River and domestic wastes input, the Bay of Annaba receives direct industrial wastes (from a great fertilizer factory) highly loaded with NH_4 (200 µM, 1.8 tons day^{-1}) and PO_4 (30 µM, 0.9 ton day^{-1}), which affect the water quality of the receiving coastal water (Ounissi et al., 2008) in particular the N:P ratio. These loading may represent about 300,000 to 400,000 inhabitant-equivalent.

These observations confirmed the findings of the correspondence analysis (CA). The factorial plan F1 x F2 of the CA provides 90.2 % of the total inertia, where the first factor (F1) contributes 66.2 % and the second factor (F2) 24 % (Figure 30). The first factor is mainly explained by the variables NH_4, PO_4 and $Si(OH)_4$:DIN, which are associated with Seybouse and Mafragh estuary observation. The Seybouse discharge was characterized by high level of NH_4 and DIN, as opposed to the Mafragh waters that were richer in $Si(OH)_4$ and NO_3, and with high $Si(OH)_4$:DIN ratios.

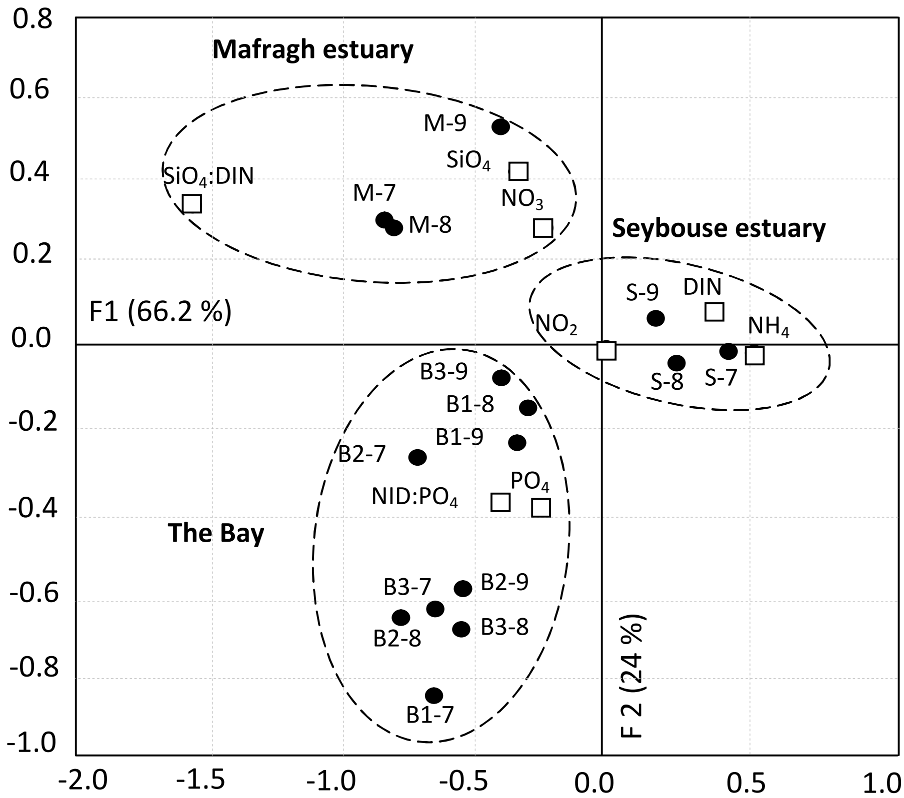

Figure 30: Factorial plan projection 1x2 of the correspondence analysis showing the three segregated areas: relative to F1, the Seybouse estuary with high DIN forms level opposed to the Mafragh estuary characterized by high levels in SiO_4, NO_3 and elevated SiO_4:DIN ratio and according to the F2, the Bay stations are both contrast to estuarine chemical features. The variables are: NH_4; NO_2; NO_3; DIN; PO_4; SiO_4; SiO_4:DIN; DIN:PO_4. The objects or sites surveyed in the years 2007; 2008 and 2009 are designed as follow: S-7; S-8; S-9: the Seybouse estuary outlet for respectively the years 2007; 2008 and 2009; M-7; M-8; M-9: the Mafragh estuary outlet for respectively the years 2007; 2008 and 2009; B1-7; B1-8; B1-9; B2-7; B2-8; B2-9; B3-7; B3-8; B3-9: the stations of the Bay B1; B2; B3 surveyed in the years 2007; 2008 and 2009.

These two continental nutrient sources also stand in contrast to the DIN:PO_4 ratio, which was lower in Mafragh estuarine inputs. The second factor is explained mainly by the levels of $Si(OH)_4$ and the $Si(OH)_4$:DIN ratio as distributed in the Mafragh estuary and in the Bay. The Mafragh estuary contributes to explain the F2 because of its high $Si(OH)_4$ levels and $Si(OH)_4$:DIN ratio. These features are opposed to the coastal waters, that are richer in DIN than PO_4 and their DIN:PO_4 ratio is more under the influence of the Seybouse estuary, which is strongly enriched by DIN and NH_4 (Figure 30). Overall, the first factor may represent the anthropogenic effects from Seybouse estuary with its heavy load of DIN and PO_4 and low $Si(OH)_4$ due to damming, as has been reported in contiguous catchments (Ounissi and Bouchareb, 2013). The second factor may represent the effect of the Mafragh estuary, which seems to play a positive role by enriching the adjacent coastal waters. However, the Seybouse estuary clearly affected the quality of the major contiguous marine waters because of the eastward current (Figure 15) that brings the water mass to the eastern part of the Bay (Ounissi and Fréhi, 1999).

In addition, there was obvious inter-annual variability in nutrient levels as well as seasonal cycles at all spatial scales. These variations in coastal nutrient followed the hydrological cycle of estuarine nutrient and water discharge. The wet years of 2007 and 2009 had more elevated nutrient values and in water discharge while the salinity values decreased significantly according to the freshwater inputs. In the wet years, the Redfield ratios were also more balanced especially for DIN:PO_4 which decreased to 16 and 20 within the estuarine plumes of Seybouse and Mafragh, respectively. These hydrological conditions did not clearly affect the $Si(OH)_4$:DIN ratio, which remained near the standard Redfield ratio value (1:1). This suggests that the continental inputs in the wet periods were more enriched in DIN over $Si(OH)_4$ and that $Si(OH)_4$:DIN increased in the dry years. In the inner Bay, Fréhi et al. (2007) and Ounissi and Fréhi (1999) reported that the estuarine discharge delivered more DIN than $Si(OH)_4$, which lead to the appearance of harmful species such as Dinophysis spp. and Alexandrium spp., despite the spring bloom of Noctiluca miliaris and other protists such as the Tintinnids Favella spp.

4. References

Avilés, A., Niell, F.X., 2007. The control of a small dam in nutrient inputs to a hypertrophic estuary in a Mediterranean climate. Water Air Soil Pollut., 180(1-4): 97-108.

Bachari-Houma, F., 2009. Modélisation et cartographie de la pollution marine et de la bathymétrie (côtes d'Alger) {partir de l'imagerie satellitaire. Thèse de doctorat, Université du Val de Marne Paris XII, Paris, pp. 257.

Bellos, D., Sawidis, T., Tsekos, I., 2004. Nutrient chemistry of River Pinios (Thessalia, Greece). Environ. Int., 30: 105-115.

Bergametti, G., Dutot, A. L., Buart-Menard, P., Losno, R., and Remoudaki E., 1989. Seasonal variability of elemental composition of atmospheric aerosol particles over the Northwestern Mediterranean. Tellus, 41b: 353-361.

Billen, G., Garnier, J., 2007. River basin nutrient delivery to the coastal sea: assessing its potential to sustain new production of non siliceous algae. Mar. Chem., 106: 148-160.

Billen, G., Garnier, J., 1999. Nitrogen transfers through the Seine drainage network: a budget based on the application of the Riverstrahler model. Hydrobiologia, 410: 139–150.

Canton, M., Anschutz, P., Poirier, D., Chassagne, R., Deborde, J., Savoye, N., 2012. The buffering capacity of a small estuary on nutrient fluxes originating from its catchment (Leyre estuary, SW France). Estuar. Coast. Shelf S., 99: 171-181.

Chester, R., Nimmo, M., Alarcon, M., Saydam, C., Murphy, K. J. T., Sanders, G. S., and Corcoran, P., 1993. Defining the chemical character of aerosols from the atmosphere of the Mediterranean-Sea and surrounding regions. Oceanologica Acta, 16: 231-246.

Conley, D.J., 2002. Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochem. Cy. 16(4): 8. DOI.org/10.1029/2002gb001894.

Conley, D.J., Stalnacke, P., Pitkanen, H., Wilander, A., 2000. The transport and retention of dissolved silicate by Rivers in Sweden and Finland. Limnol. Oceanogr., 45(8): 850-853.

Cozzi, S., Giani, M., 2011. River water and nutrient discharges in the Northern Adriatic Sea: Current importance and long term changes. Cont. Shelf Res., 31: 1881-1893.

Daly-Yahia-Kafi, O., Souissi, S., Gomez, F., Daly-Yahia, M.N., 2005. Spatio-temporal distribution of the dominant Diatom and Dinoflagellate species in the Bay of Tunis (S.W. Mediterranean Sea). Medit. Mar. Sci., 6(1): 17-34.

Diaz, F., Naudin, J.J., Courties, C., Rimmelin, P., Oriol, L., 2008. Biogeochemical and ecological functioning of the low-salinity water lenses in the region of the Rhone River freshwater influence, NW Mediterranean Sea. Cont. Shelf Res., 28: 1511-1526.

Dulac, F., Buart-Menard, P., Arnold, M., Ezat, U., and Martin D., 1987. Atmospheric input of trace metals to the Western Mediterranean sea: 1. Factors controlling the variability of atmospheric concentrations. J. Geophys. Res., 92: 8437-8453.

European Environment Agency (EEA)., 1999. State and pressures of the marine and coastal Mediterranean environment. Environmental assessment series. Office for Official Publications/EE, L-2985 Luxembourg, 5: 137p.

European Environment Agency (EEA)., 2007. Waterbase, v7. Available from: http://dataservice.eea.europa.eu/dataservice/metadetails.

Flo, E., Garcés, E., Manzanera, M., Camp, J., 2011. Coastal inshore waters in the NW Mediterranean: Physicochemical and biological characterization and management implications. Estuar., Coast. Shelf Res., 93: 279-289.

Fréhi, H., Couté, A., Mascarell, G., Perrette-Gallet, C., Ayada, M., Kara, M.H., 2007. Dinoflagellés toxiques et/ou responsables de blooms dans la baie d'Annaba (Algérie). C. R. Biol., 330: 615-628.

Ganor, E., and Mamane Y., 1982. Transport of Saharan dust across the eastern Mediterranean. Atmos. Environ., 16: 581-587.

Ganor, E., Levin, Z., and Van Grieken, R., 1998. Composition of individual aerosol particles above the Israelian Mediterranean coast during the summer time, Atmos. Environ., 32, 1631-1642

Garcia-Esteves, J., Ludwig, W., Kerherve, P., Probst, J.L., Lespinas, F., 2007. Predicting the impact of land use on the major element and nutrient fluxes in coastal Mediterranean Rivers: The case of the Tèt River (Southern France). Appl. Geochem. 22, 230-248.

Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loye-Pilot, M-D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Saydam, C., Soudine, A. and Ziveri, P., 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea, Prog. Oceanogr., 44: 147-190.

Gullu, G., Olmez, I., Aygun, S., and Tuncel, G., 1998. Atmospheric trace element concentrations over the Eastern Mediterranean sea: factors affecting temporal variability, J. Geophysical Research, 103: 21943-21954.

Hallas, M.K., Huettel, M., 2013. Bar-built estuary as a buffer for riverine silicate discharge to the coastal ocean. Cont. Shelf Res., 55: 76-85.

Herut, B., Krom,M. D., Pan, G., andMortimer, R. 1999. Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: sources, fluxes and possible impact, Limnol. Oceanorg., 44: 1683–1692.

Humborg, C., Conley, D.J., Rahm, L., Wulff, F., Cociasu, A., Ittekot, V., 2000. Silicon retention in River basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. Ambio, 29: 45-51.

Humborg, C., Pastuszak, M., Aigars, J., Siegmund, H., Morth, C.M., Ittekot, V., 2006. Decreased silica land-sea fluxes through damming in the Baltic Sea catchment. Significance of particle trapping and hydrological alterations. Biogeochemistry, 77: 265-281.

Ibáñez, C., Prat, N., Duran, C., Pardos, M., Munne, A., Andreu, R., Caiola, N., Cid, N., Hampel, H., Sanchez, R., Trobajo, R., 2008. Changes in dissolved nutrients in the lower Ebro River: Causes and consequences. Limnetica, 27(1): 131-142.

Khélifi-Touhami, M., Ounissi, M., Saker, I., Haridi, A., Djorfi, S., Abdenour, C., 2006. The hydrology of Mafragh estuary (Algeria): Transport of inorganic nitrogen and phosphorus to the adjacent coast. J. Food Agric. Environ. 4(2): 340-346.

Koçak, M., Kubilay, N., Tugrul, S., Mihalopoulos, N., 2010. Long-term atmospheric nutrient inputs to the Eastern Mediterranean: sources, solubility and comparison with riverine inputs. Biogeosciences Discuss., 7: 5081–5117.

Kubilay, N. and Saydam, C., 1995. Trace elements in atmospheric particulates over the Eastern Mediterranean: concentration, sources and temporal variability, Atmos. Environ., 29: 2289–2300.

Kucuksezgin, F., Kontas, A., Altay, O., Uluturhan, E., Darilmaz, E., 2006. Assessment of marine pollution in Izmir Bay: Nutrient, heavy metal and total hydrocarbon concentrations. Environ. Int. 32: 41-51.

Ludwig, W., Dumont, E., Meybeck, M., Heussner, S., 2009. River discharges of water and nutrients to the Mediterranean and Black Sea: major drivers for ecosystem changes during past and future decades. Prog. Oceanogr. 80, 199–217, DOI.org/10.1016/j.pocean.2009.02.001.

Markaki, Z., Oikonomou, K., Koc¸ak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., and Mihalopoulos, N. 2003: Atmospheric deposition of inorganic phosphorus in the Levantine basin, eastern Mediterranean: spatial and temporal variability and its role in seawater productivity, Limnol. Oceanorg., 48: 1557–1568.

Markaki, Z., Loÿe-Pilot, M.D., Violaki, K., Benyahya, L.b., Mihalopoulos, N. 2008. Variability of atmospheric deposition of dissolved nitrogen and phosphorus in the Mediterranean and possible link to the anomalous seawater N/P ratio. Mar. Chem. DOI:10.1016/j.marchem.2008.10.005

Meybeck, M., Vörösmarty, C., 2005. Fluvial filtering of land-to-ocean fluxes: from natural Holocene variations to Anthropocene. C. R. Geoscience, 337: 107-123.

Nikolaidis, N.P., Karageorgis, A.P., Kapsimalis, V., Drakopoulou, P., Skoulikidis, N., Behrendt, H., Levkov, Z., 2009. Management of nutrient emissions of Axios River catchment: their effect in the coastal zone of Thermaikos Gulf, Greece. Ecol. Model., 220(3): 383-396.

Ounissi, M., Frehi, H., 1999. Variability of microphytoplankton and Tintinnida (ciliated protozoa) in an eutrophic sector of the Annaba Gulf (S.W. Mediterranean). Cah. Biol. Mar., 40(2): 141-153.

Ounissi, M., Khammar, H., Ziouch, O., Saker, I., Haridi, A., Khelifi-Touhami, M., Abdenour, C., 2008. Apports d'azote et de phosphate au littoral d'Annaba par les effluents urbains, industriels et par la rivière Seybouse (Algérie). In: International Conference on rapid urbanisation and land use conflicts in coastal cities, Chouikhi, A., Zibdah, A., Khalaf, A. (Eds.), INOC, Izmir, Turkey, 13, pp. 181-186.

Ounissi, M, Bouchareb, N., 2013. Nutrient distribution and fluxes from three Mediterranean coastal Rivers (NE Algeria) under large damming. C. R. Geoscience 345: 81-92. DOI.org/10.1016/j.crte.2013.02.002.

Samson-Kechacha, F.L., 1981. Variations saisonnières des matières nutritives de la Baie d'Alger: Recherche des facteurs contrôlant le développement du phytoplancton. Thèse de Doctorat 3e cycle, Université STHB, Alger, pp. 98.

Sebilo, M., Billen, G., Grably, M., Mariotti, A., 2003. Isotopic composition of nitrate-nitrogen as a marker of riparian and benthic denitrification at the scale of the whole Seine River system. Biogeochemistry, 63:35-51.

Suzal, A., Bizsel, N., Bizsel, K.C., Husrevoglu, Y.S., 2008. Dissolved Nutrient Behaviour along the Estuarine Salinity Gradient at the Gediz River Mouth (Aegean Sea, Turkey). Turkish J. Eng. Env. Sci., 32: 67-84.

Sylaios, G., Koutrakis, E., Kallianiotis, A., 2006. Hydrographic variability, nutrient distribution and water mass dynamics in Strymonikos Gulf (Northern Greece). Cont. Shelf Res. 26, 217-235. Turley, C.M., 1999. The changing Mediterranean Sea-a sensitive ecosystem? Prog. Oceanogr., 44 : 387-400.

Torrecilla, N.J., Galve, J.P., Zaera, L.G., Retamar, J.F., Alvarez, A.N.A., 2005. Nutrient sources and dynamics in a Mediterranean fluvial regime (Ebro River,NE Spain) and their implications for water management. J. Hydrol., 304: 166-182.

Violaki, K., Zarbas, P., Mihalopoulos, N., 2010. Long-term measurements of dissolved organic nitrogen (DON) in atmospheric deposition in the Eastern Mediterranean: Fluxes, origin and biogeochemical implications. Mar. Chem., 120: 179–186

Conclusion

Conclusions

This work provides, for the first time, the distribution and nutrient loads of two important Algerian estuaries and nutrient loads from wet atmospheric deposition and their impact on the receiving coastal water quality. The fundamental results may be summarized in the following bullets:

- The Seybouse estuary inputs were rich in PO_4 and NH_4 compared to other Mediterranean Rivers, where NO_3 generally dominates.
- The DIN-specific loadings from the Seybouse outlet may be considered among the highest of Mediterranean Rivers. Both estuaries' outlets were impoverished in $Si(OH)_4$ because of the estuarine buffering and retention by reservoirs.
- The quality of the water that was introduced into the Bay of Annaba was also reflected in the unbalanced Redfield molar ratios. The $Si(OH)_4$:DIN ratio for Seybouse waters was low in all seasons, rarely exceeding 0.5, in contrast to the Mafragh waters which had consistently balanced $Si(OH)_4$:DIN.
- The lowering of $Si(OH)_4$ levels in the Mafragh estuary did not affect the $Si(OH)_4$:DIN ratio, which remained almost balanced because DIN inputs were limited in this more pristine watershed.
- The Mafragh estuary may be a good example of $Si(OH)_4$:DIN molar ratio that is mainly controlled by human nitrogen inputs rather than retention in estuaries or reservoirs.
- Therefore, controlling nitrogen inputs in catchments seems to be of primary importance compared to lowering by dam construction to allow more Si passage, in particular for Mediterranean sub-arid regions.
- The Mafragh estuary appears to be less impacted in terms of NH_4 and PO_4; it can play a positive role by introducing clean waters that may mitigate the highly polluted Seybouse inputs.
- In wet years, the Redfield ratios were more balanced in the inner Bay stations.
- At the marine stations, because of estuarine inputs, the N:P and Si:N ratios were below the Redfield standard values in 60 % of samples.
- By contrast to the most Mediterranean coastal zones, the Bay of Annaba receives low nutrient inputs from wet atmospheric deposition, which contribute only by 2-3 % according to the nutrient.
- Also, their nutrient molar ratios were found largely disturbed (N:P = 28; Si:N = 0.34), which could modulate, in some extent, the coastal eutrophication nuisance.

List of abbreviations

List of abbreviations

NH_4^+: Ammonium ion 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^{3-}: Phosphate ion also noted PO_4
$Si(OH)_4$: Silicic acid noted SiO_4
N: Nitrogen
P: Phosphorus
Si: Silicon
CO2: Carbon dioxide
Si/C: Silicon to carbon ratio
Si/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
AFC : Factorial Correspondence Analysis
μM : Micromol per liter or $\mu mol\ l^{-1}$
UAN: solution of Urea and Ammonium Nitrate in water
IGBP: International Geosphere-Biosphere Programme
GIWA: Global International Waters Assessment
LOICZ: Land-Ocean Interactions in the Coastal Zone
MESRS: Ministry of Higher Education and Scientific Research

Article

Variability of the dissolved nutrient (N, P, Si) concentrations in the Bay of Annaba in relation to the inputs of the Seybouse and Mafragh estuaries

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Variability of the dissolved nutrient (N, P, Si) concentrations in the Bay of Annaba in relation to the inputs of the Seybouse and Mafragh estuaries

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ABSTRACT

Dissolved inorganic nitrogen (DIN), phosphate (PO_4) and silicic acid ($Si(OH)_4$) loads from the Seybouse and the Mafragh estuaries into the Bay of Annaba, Algeria, were assessed at three stations of the Bay over three years. The Seybouse inputs had high levels of DIN and PO_4, in contrast to the Mafragh estuary's near-pristine inputs; $Si(OH)_4$ levels were low in both estuaries. The DIN:PO_4 molar ratios were over 30 in most samples and the $Si(OH)_4$:DIN ratio was less than 0.5 in the Seybouse waters, but nearly balanced in the Mafragh. The specific fluxes of Si–$Si(OH)_4$ (400–540 kg Si km^{-2} yr^{-1}) were comparable in the two catchments, but those of DIN were several-fold higher in the Seybouse (373 kg N km^{-2} yr^{-1}). The inner Bay affected by the Seybouse inputs had high levels of all nutrients, while the Mafragh plume and the outer marine station were less enriched.

1. Introduction

Coastal zones and their resources are important contributors to economic development and quality life. Their exploitation represents a significant source of income for coastal people, through fisheries, agriculture and tourism. Therefore, their preservation is a first-order priority for stable socio-economic development in the Mediterranean region (Turley, 1999). In oligotrophic seas such as the Mediterranean Sea, nutrient from rivers play a critical role in sustaining the marine productivity, and zones of high productivity are mainly limited to the coastal waters that receive major freshwater inputs (Bosc et al., 2004). For rivers that feed the Mediterranean Sea, Ludwig et al. (2009) reported that fluxes of N and P were strongly enhanced by anthropogenic sources and that their total inputs to the Mediterranean Sea may have increased by a factor >5. In contrast, a decrease in dissolved silica (Si) may be expected. It is strongly controlled by water discharge and also potentially reduced by river damming. Humborg et al. (2000) reported that Si limitation may expand in the Mediterranean Rivers over recent decades, and dissolved Si concentrations have been reduced to less than half their pre-dam construction values in the Danube and Nile Rivers. They also concluded that the dramatic changes in nutrient loads and composition (Si:N:P ratios) entering coastal seas will have far-reaching effects on coastal ecosystems. Turner et al. (1998) described how freshwater and marine ecosystems can undergo fundamental aquatic food web changes as diatom growth is compromised when the Si:DIN ratio falls below 1:1.

Therefore, a key topic of coastal research now centers around changes in the ratios and loading of N, P, and Si and their effects on phytoplankton composition (Béthoux et al., 2002; Cloern, 2001; Howarth and Marino, 2006; Justic et al., 1995). However, the study of river syndromes at a global or regional scale is still limited by the available information (Meybeck, 2003) and impacts of some river syndromes on aquatic resources are already considered as a first priority.

Data on river nutrient loading to the Mediterranean basin are scarce and are missing for many eastern and North African countries, so the general picture is biased (Ibáñez et al., 2008; Ludwig et al., 2009; Milliman, 2007). In Algeria, despite the notable lack of data on nutrient loads from river watersheds to the receiving shelf, there has been no research until now on the distribution of dissolved nutrients in coastal areas in relation to river inputs. For the Bay of Annaba, the few published data are very limited in temporal and spatial scales, and they address only the distribution of the inorganic nitrogen and phosphate in the inner sector of the Bay of Annaba (Frehi et al., 2007; Ounissi and Frehi, 1999) and seasonal fluxes of the same nutrients from the Mafragh estuary (Khélifi-Touhami et al., 2006). The Bay of Annaba receives diffuse inputs from the Seybouse and the Mafragh estuaries in addition to direct urban and industrial wastes. The estuary' watersheds cover approximately 10,000 km^2 and together house over two million people, for whom intense agricultural practices have become the most important economic activity in the last decade. The population increases and its activities and anthropogenic activity have increased inputs from household waste,

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and a large amount of water is now retained by dams (Ounissi and Bouchareb, 2013) for irrigation. Fertilizer use can also induce changes in the functioning of the adjacent coastal ecosystem. The Seybouse estuary is major contributor of nutrient inputs to the coastal waters. The industrial waste from a large fertilizer factory delivers over 1 million $m^3\ d^{-1}$ of water that is heavily loaded with ammonium and phosphate (Ounissi et al., 2008). Moreover, untreated domestic waste delivers approximately 0.3 million m^3 of water with heavy ammonium and phosphate loads. Human influences and an irregular hydrological regime are the common features in Mediterranean River systems, which affect both coastal and inland water characteristics.

The objectives of the present study were (1) to estimate nutrient (N, P and Si) fluxes from the Seybouse and Mafragh estuaries and (2) to assess how much that transfer influences the temporal and spatial distribution of nutrient levels and ratios in the Bay of Annaba.

2. Sampling sites and methods

2.1. Sampling sites

In the Bay of Annaba, the Modified Atlantic Water current (MAW) moves eastward from the marine side (Millot and Taupier-Letage, 2005) and crosses the shelf of Annaba (Fig. 1), which allows some renewing of the outer neritic waters (Ounissi and Frehi, 1999). However, the inner part of the bay mostly influenced by continental inputs from the Seybouse and the Mafragh estuaries (Fig. 1) and urban waste of the roughly one million people in the city of Annaba and its surrounding villages. Moreover, industrial waste from a single large fertilizer factory deposited over a million $m^3\ d^{-1}$ heavily loaded with nitrogen and phosphorus compounds.

Except during the winter wet season, when rivers discharge freshwater into the bay, the Seybouse and Mafragh Rivers are tidal estuaries, with large seasonal fluctuations in their salt water intrusion. The Mafragh and Seybouse appear as atypical estuaries with the hydrologic cycle comprising river phase, estuarine core phase and lagoonal phase (Khélifi-Touhami et al., 2006). The duration of each phase may strongly vary with the river input and the duration of dry season (Fig. 2). The Mafragh estuary's mouth might be closed from its tidal connection under extended period of dry years. Following periods of high rainfall (winter and in the beginning of spring) and freshwater runoff, the volume of the estuary is entirely discharged into the sea, and the salt wedge is then retreated to the coast in a few days. From the middle spring to the end of autumn, the estuary is dominated by tidal advection, and

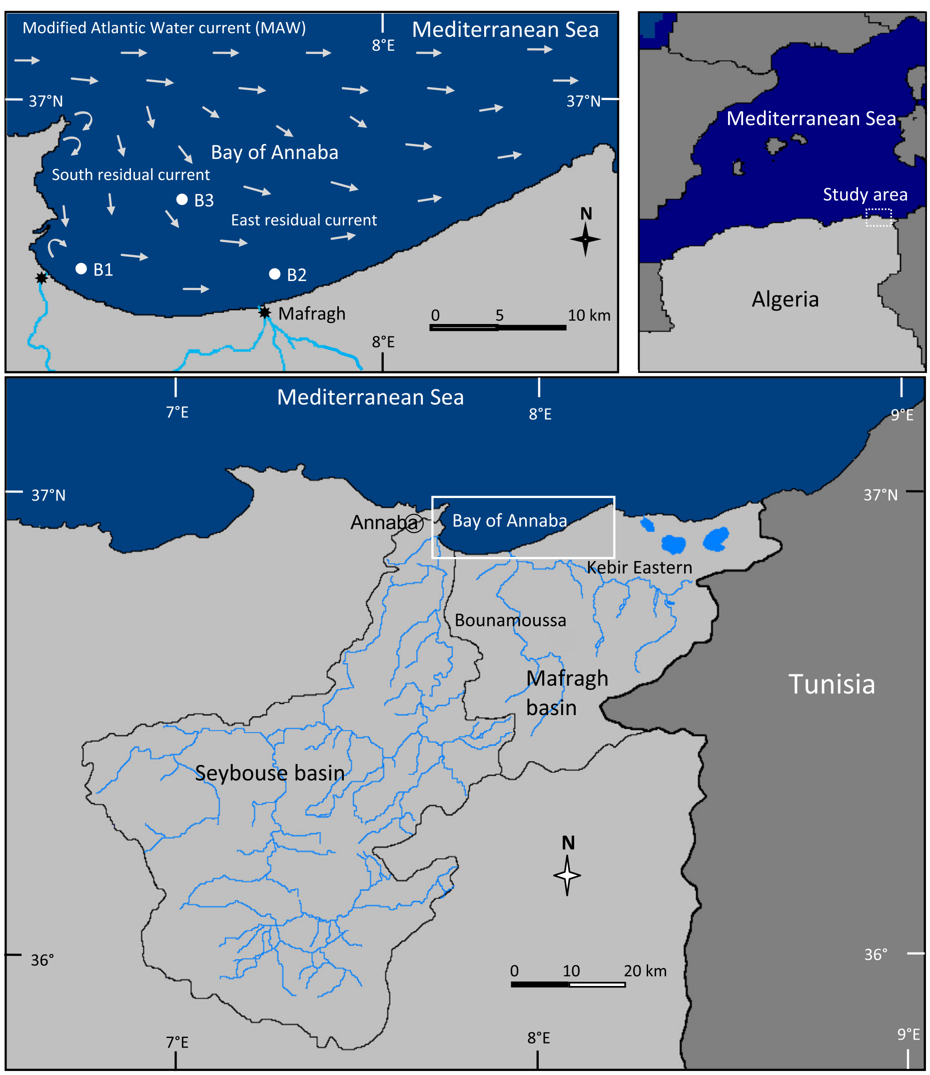

Fig. 1. Map of the Seybouse and Mafragh rivers' catchments and the adjacent coastal area showing the sampling sites at the estuaries' outlets (*), and the Bay of Annaba (B1; B2 and B3).

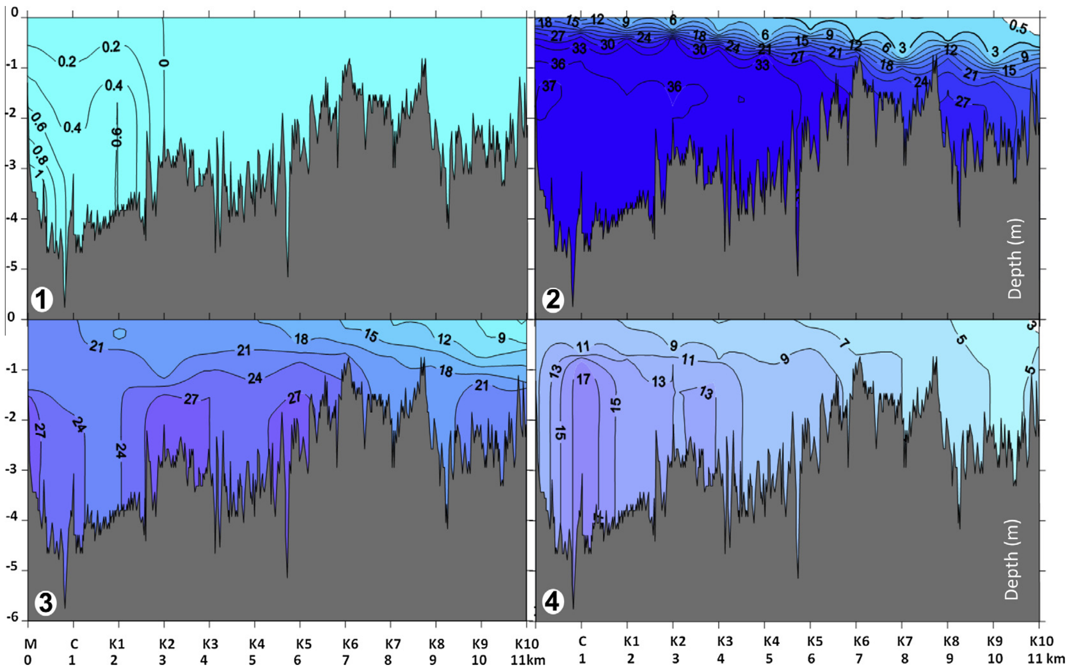

Fig. 2. Salinity profiles (pss) for the Mafragh estuary (Kebir western branch) in 2006, from the mouth (M), the confluence (C) of the two tributaries (Kebir western and Bounamoussa) up to 11 km inland (K1–K11). 1: winter, 2: spring, 3: summer, 4: autumn.

expands in a very stratified system, with two layers (Fig. 2), in which the saltwater layer occupies over 80% of the water column.

The saltwater wedges in the two rivers reach up 8 and 15 km respectively (Khélifi-Touhami et al., 2006).

The population density in the Seybouse basin (6470 km^2) is approximately 220 inhab. km^{-2}, while the Mafragh basin (3200 km^2) is less populated (80 inhab. km^{-2}). Intensive agricultural activity has become the primary land use, and the watersheds are now largely regulated by multiple dams that retain approximately one third (Mafragh) to one half (Seybouse) of the total annual runoff. The Mafragh watershed is, however, distinguished by its large virgin wetlands in the lower reaches, which may act as a buffer for contamination and flood events. In contrast, because of high population density, intensive agriculture and industrialization, the Seybouse is one of the most polluted rivers in Algeria.

Sites for spatial data were selected by purposive sampling using maximum variation technique (Scherrer, 1984). On the shelf of Annaba, three sampling stations were chosen according to the importance of external influences (Fig. 1): the coastal area submitted to the Seybouse estuary plume (Inner Bay, station B1, 6 m depth); the coastal area near the Mafragh estuary (inner Bay, station B2, 19 m depth) and the central Bay far from continental influence and mostly subject to the MAW intrusion (outer water, B3, 40 m depth). To assess the influence of estuarine inputs, the Seybouse and the Mafragh estuaries were sampled at their respective outlet stations.

2.2. Analytical methods

As we collected water samples, we also measured the flow velocity from the outlet' stations of the Seybouse and Mafragh estuaries with CM-2 current meter, Toho Dentan Co., Ltd., Tokyo. Water salinity and temperature measurements were taken with a multi-parameter probe, WTW 197i. As mentioned by the manufacturer, the precisions of the salinity and the temperature measurements, are respectively ±0.1 pss and ±0.1 °C. The flow rate ($m^3\ s^{-1}$) was calculated by multiplying the water velocity ($m\ s^{-1}$) by the total surface area (m^2) of a transect of the estuary' at the outlet' stations. However, the estimation of the freshwater inputs from highly dynamic and atypical estuarine systems was not easy to carry out. This suggests some explanations. For example, the estuarine part varies with the season from 0 to 7 km in the Seybouse River estuary, and from 0 to 20 km in the Mafragh River estuary (Fig. 3B). If we measure nutrient concentrations and water discharge at 7 km in the Seybouse River estuary, where the salinity is near 0 pss (freshwater), we estimate here what is introduced to the estuary. By the opposite, when we determine water discharge at the mouth, we always measure what is introduced to the sea from the estuary in dry season and from the River in wet season. The problem now is how to estimate the amount of the fresh water discharged, from the estuary, into the sea in such highly dynamic systems. The tide in the estuaries is semidiurnal and microtidal, where the ebb and flood phases duration vary largely. Depending on river flow in particular, the flood phase fluctuates between 0 and 6 h, and the ebb tide one varies between 6 and 24 h (but the discharge may continue for several days because the tide regime is masked by high river flow). The other constraint is the depth of the fresh water layer. We determine at each sampling the periods of the tidal phase, and the fresh water layer as can be seen in Fig. 3A. The measurements of salinity were taken vertically each 10 cm. For example, in May (purple[1] circle), the freshwater layer is about 45 cm; April: 190 cm (black circle); August: 0 cm (blue circle), and so on (Fig. 3A). Having the current velocity, the freshwater layer, the ebb tide phase duration, we can determine the estuarine inputs.

Two liters of water from the middle of the flow were collected for nutrient analysis. Surface water samples were taken in the estuaries monthly from January 2007 to December 2009 and from March 2007 to December 2009 in the Bay of Annaba. The Seybouse estuary was only sampled twice in the years 2008 and 2009. Due to bad weather in the Bay of Annaba, we were unable to collect several samples: May 2007; March; September and November 2008;

[1] For interpretation of color in Fig. 3, the reader is referred to the web version of this article.

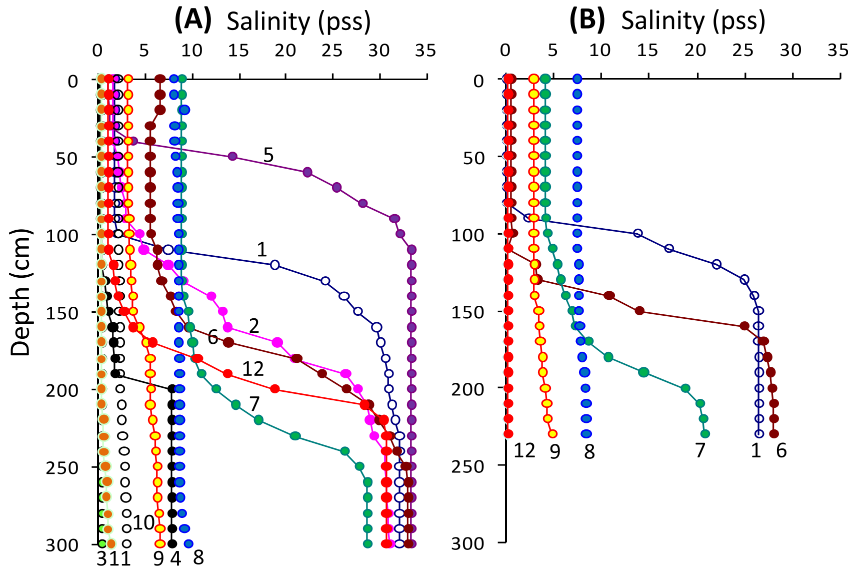

Fig. 3. Monthly vertical profiles of salinity at the outlet (A) and at 11 km from the outlet (B) of the Mafragh estuary (kebir Eastern branch), during the year 2007. The circles 1 to 12 correspond successively to the salinity profiles of January to December. In graphic B, values of 2, 3, 4, 5, 10 and 11 are near zero, and are superimposed on the depth axis.

and September 2009. In addition to surface water sampling in the Bay of Annaba, bottom waters were sampled using Niskin bottle. Water samples for nutrient analyses were frozen in polyethylene bottles and processed within 2 days of collection. In the laboratory, after filtration of the sample through a Whatman GF/C glass filter (0.5 μm porosity), all nutrient (phosphate: PO_4; ammonium: NH_4; nitrate: NO_3; nitrite: NO_2; silicic acid: $Si(OH)_4$) concentrations were determined by means of the standard colorimetric methods described by Parsons et al. (1989). Their precisions are: ±3% (PO_4), 5% (NH_4), 3% (NO_3), 2.5% (NO_2), 2.5% ($Si(OH)_4$). The instantaneous flux of nutrients was calculated by multiplying their levels by the estuary flow. The annual loads for nutrients were estimated using the method of average instantaneous loads (Preston et al., 1989):

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

where F is the annual load (tons/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.

2.3. Statistical analysis

Even though purposive sampling offers a substantial amount of information relative to the sampling effort, all estimators are subject to significant bias including correlation, mean, variance, etc. (Scherrer, 1984). In fact, the stations have been placed to collect data at strategic points (outlets and their marine plumes and the outer marine station affected by the MAW current) or to find possible gradients.

The intentional placement of the stations may be responsible for correlations between nutrients and spatiotemporal variability, but these factors have not been considered in this work. However, data issued from purposive sampling can reveal interesting findings when used in multivariate factorial analyses, especially in environmental diagnosis and to find trends along spatial gradient of the variables (Scherrer, 1984). A correspondence analysis (CA) multivariate technique was then used to determine any possible co-variation between inorganic nutrients and their ratios, both in the estuaries' outlets and at the coastal stations, during the three years of surveys. The CA has several advantages compared to multivariate techniques such as principal component analysis (PCA), and it is more appropriate for the data we collected. Presenting the variables and objects together in a biplot graphic, facilitates the interpretation of the cloud points and their associations. In addition, the CA is a double principal component analysis on the variables (columns) and objects (rows) and also compares rows or columns using the Chi-square distance, which offers a superior method of weighting the individual data. In addition, the data do not need to be normalized, a procedure that can distort reality as it does for PCA (Dervin, 1988). The statistical software Statistica, 2008 was used to perform the CA. The contingency table analyzed with CA is a matrix of the annual averages of 8 nutrient levels and ratios (variables) observed on 15 spatiotemporal situations (objects) representing the two outlets and three coastal stations over three years of survey (2007–2009).

3. Results

3.1. Hydrology and nutrient variability and fluxes at the estuaries' outlets

The hydrological parameters recorded in the two estuaries are given in Fig. 4. The estuarine water flow at the respective outlets varied according to the precipitation, especially for the Seybouse estuary, where discharges in 2009 were 6-fold higher than those of 2008 (Fig. 4). Because of the large marshland supplying the Mafragh estuary, discharges varied less and seem to be more important than those of Seybouse (Fig. 4). In the Mafragh the inter-annual variability was mitigated, and did not exceed 4-fold because the surrounding wetlands regulate flow. As seen in Fig. 4, the minimum flow was recorded in 2008 because of the low rainfall, as it was for the Seybouse basin. The water temperature varied in the same range in both estuaries, but the annual average value of Seybouse waters was significantly higher because of the amount of wastewater from human population.

In the outlets of the estuaries, the salinity is controlled by river inputs and to a lesser degree by tidal intrusion. In the wet period which extends approximately from November to April, continental

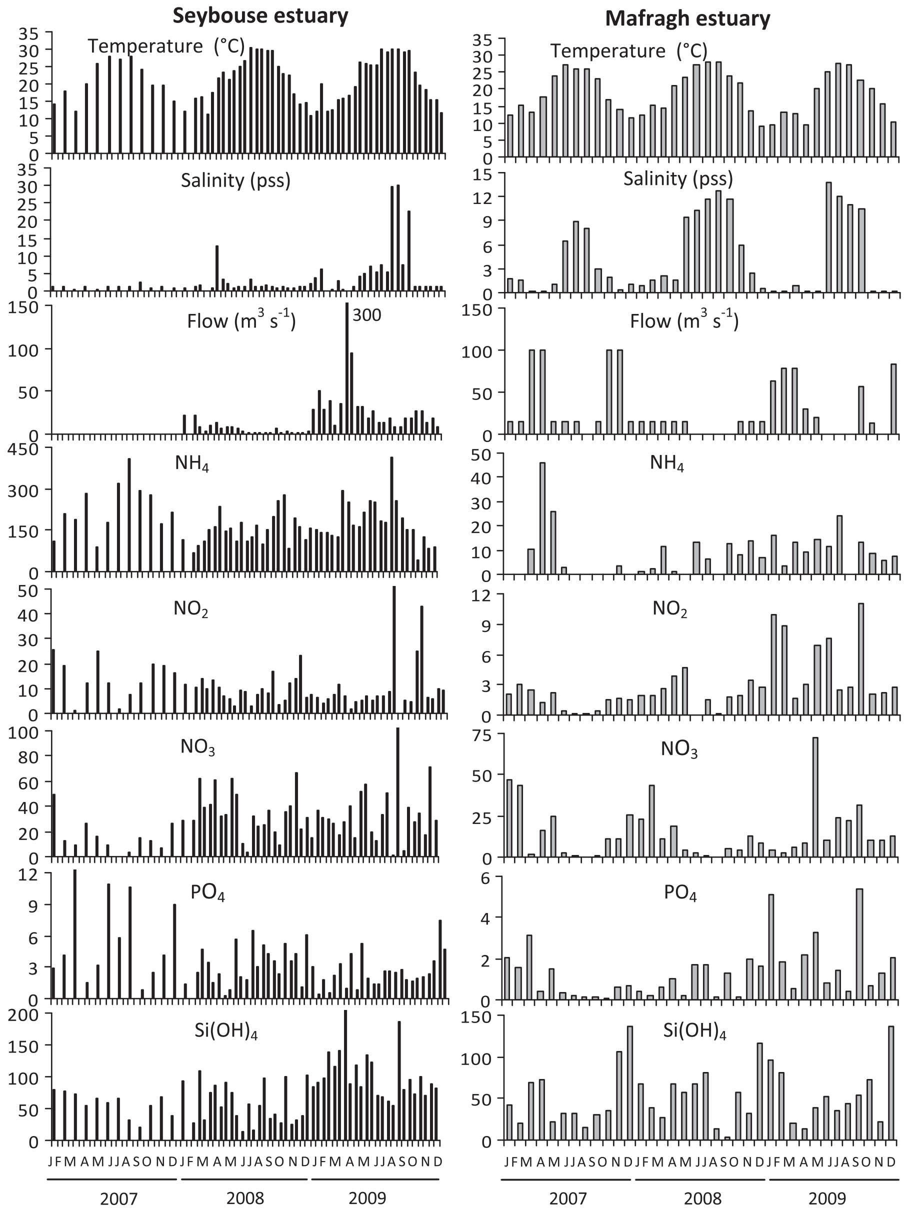

Fig. 4. Seasonal variations in temperature, salinity, flow and nutrient levels (μM) in the Seybouse and Mafragh estuaries, January 2007–December 2009. Note that there are no flow measurements for the Seybouse estuary in 2007.

inputs dominated the entire estuary, driving the salt wedge back towards the sea. Salinity values then decreased to between 0.5 and 1 pss (Fig. 2a and b). During the dry periods in summer and autumn, marine intrusion dominated and increased the salinity over the entire estuarine layer. Therefore, the observed bottom salinities (not represented here) may be comparable to those of the adjacent shoreline, and the surface salinity ranged between 10 and 30 pss. In the spring and summer, the estuaries were marked by variable salinity depending on the tidal phase. During this period, the surface values fluctuated at some units, reflecting large marine intrusions (Fig. 4). During late summer and autumn, the marine connection of the Mafragh estuary was closed and it appeared to function as a non-tidal lagoon. There, the surface salinity increased to a maximum of 6–14 pss, depending on the historical freshwater inputs (Fig. 4).

The waters from the mouth of the Seybouse were highly charged with dissolved nitrogen forms ($DIN = NH_4 + NO_2 + NO_3$) and PO_4, and the values were higher than any from the Mafragh estuary (Fig. 4). The dominant character of the Seybouse was its high NH_4 levels which reached an average of 200–260 μM depending on the year; this represents more than 20 times the levels recorded in the outlet of the Mafragh. The oxidized forms of nitrogen, as NO_3 plus NO_2, always occurred in a low fraction compared to the NH_4, which represented more than 80% of DIN. In contrast, in the Mafragh outlet, the oxidized form of nitrogen accounted for 60%. The Seybouse estuary also had high levels of PO_4, with an average value of 2.5–6 μM, and the maximum was recorded in the year 2007. Again, the PO_4 enrichment of the Seybouse waters relative to the Mafragh was several-fold (Fig. 4). The average level in the Mafragh ranged from 1 to 2.5 μM, and the maximum was found in the unusually wet year of 2009.

The $Si(OH)_4$ levels, unlike those of DIN forms or PO_4, were low in both estuaries, particularly in the dry years of 2007 and 2008, when the average values decreased to 50 μM (Fig. 4). In the exceptionally rainy year of 2009, as seen in Fig. 4, the $Si(OH)_4$ levels increased to 100 μM and 56 μM in the Seybouse and Mafragh outlets, respectively.

Because the estuaries buffer nutrient dynamics, the seasonal variations in the outlets were masked. Average levels in the wet period were slightly higher than those of the dry season, particularly in the Seybouse. However, the levels of NO_3 and $Si(OH)_4$ increase by 20–40% in the wet period compared to the dry ones. At the Seybouse outlet, NH_4 levels were always high, but paradoxically increased by 45% in the dry season. This trend may indicate that NH_4 is largely from urban inputs.

As shown in Fig. 5, the estuaries released waters with very imbalanced Redfield ratios ($DIN:PO_4$ and $Si(OH)_4:DIN$). The disturbance is clearer for the Seybouse estuary, where $DIN:PO_4$ reached an average of 92–135 and $Si(OH)_4:DIN$ did not pass 0.5 (Fig. 5). Not only did nitrogen inputs dominate in the mouth of Seybouse, but there was also a large decrease of $Si(OH)_4$ in the upper catchment, which was likely responsible for the sharp decrease in the $Si(OH)_4:DIN$ ratio or the increase of $DIN:PO_4$. Despite the relative high $DIN:PO_4$ ratio (20.8) in the Mafragh estuary, the $Si(OH)_4:DIN$ appears to be more balanced, its average varying between 2 and 13 (Fig. 5). For both estuaries, all of these ratios were more disturbed in the dry season, when $Si(OH)_4$ levels decreased as NID and PO_4 increased.

Nutrient fluxes from the estuaries were highly variable between years, depending principally on river flow (Table 1). The Seybouse estuary introduced large amounts of all nutrients compared to the Mafragh estuary; it carried twice the oxidized nitrogen and Si–$Si(OH)_4$ and more than 20 times the N–NH_4. However, the two estuaries input comparable masses of P–PO_4. Only the Si–$Si(OH)_4$ fluxes were higher in the Mafragh estuary compared to the Seybouse, and only for the dry year of 2008. The Seybouse estuary delivered considerable fluxes of DIN in the heavy rainfall year of 2009, of which 84% were in the form of N–NH_4. In contrast, the Mafragh estuary delivered less DIN, with a high fraction of oxidized forms as seen in Table 1.

In addition, large amounts of Si–$Si(OH)_4$ were loaded from the estuaries in 2009 in their respective high flows. The maximum specific loading of DIN was on the order of 700 kg N km^{-2} yr^{-1} in the Seybouse outlet and only approximately 150 kg N km^{-2} yr^{-1} in the Mafragh. However, Si–$Si(OH)_4$ loading of the two watersheds was remarkably comparable in wet years (approximately 750 kg N km^{-2} yr^{-1}) and within several tens kg N km^{-2} yr^{-1} in dry years (Table 1). The P–PO_4 specific loadings were found important, ranging from 1 to 15 kg N km^{-2} yr^{-1} according to the year. Most of these loadings occurred in winter coinciding with agricultural soil amendment. Because they were almost closed, the outlets delivered fewer nutrients in the rest of the year. In addition to the high masses introduced to the bay via Seybouse, the loading ratios $DIN:PO_4$ and $Si(OH)_4:DIN$, were also unbalanced. The $DIN:PO_4$ ratio was above 30 and the $Si(OH)_4:DIN$ was below 1.

3.2. Hydrology and nutrient variability in the bay

The temperature ranged between 12 °C and 28 °C, with a minimum in February, a maximum in August and an average value of 19–21 °C, depending on the station. Through the seasons and years, the surface salinity fluctuated between 23 and 37.9 pss (Fig. 6). The lowest salinity values were recorded at the inner station B1, located at the Seybouse plume, and their averages varied in the range of 32–36.4 pss. The other inner station, B2 of the Mafragh plume, showed comparable but elevated surface values ranging from 34 to 36.8 pss (Fig. 6). Surface salinity values increased to 36.5–37 pss in the outer coastal waters (station B3) but remain stable throughout the seasons. Here, freshwater influences were so limited that the salinity deviation did not exceed 0.5 pss (Fig. 6), a value that reflects the major hydrological features of the Modified Atlantic Water (MAW) that prevails the Bay of Annaba. The estuarine influence on coastal waters was also expressed by the stratification in the shallower waters of station B1 and to a lesser extent in station B2. These influences did not reach the outer waters of station B3 because of thorough mixing and a constant salinity through the entire water layer (Fig. 6). Instead, this area is under the influence of external waters via the residual current of MAW penetrating the Bay.

Station B1 directly reflected to the Seybouse inputs and showed the highest levels in all nutrients, as shown in Fig. 6. Through the years the DIN surface levels remain almost unchanged, fluctuating around 10 μM in the Seybouse plume, and NH_4 is the main fraction of DIN. Only the rainy year of 2009 showed significantly elevated values (Fig. 6). Station B2 corresponds to the Mafragh plume, and the DIN levels were half those of station B1, with the NH_4 proportion still forming the essential part of DIN. Station B3 had the least DIN, which reflects the characteristics of external waters. The NH_4 fraction was the dominant form within DIN of surface waters (Fig. 6). Large amounts in DIN appeared in winter after the continental inputs (Fig. 6). At times the DIN levels were lower, especially in the surface waters at station B3, but in no season were they depleted. Even if NO_3 ions are known to originate from river discharges, their levels in the Bay throughout the year are only in the order of 1 μM in station B2 and B3 and 3 μM in the Seybouse plume (B1). Dilution effects undoubtedly lowered the levels of this nutrient because its level in the Seybouse inputs was about 30 μM. Because of the high hydrodynamic forcing that induces thorough mixing in winter and spring, the water column in the shallower waters of station B1 showed the same DIN levels. The other deeper

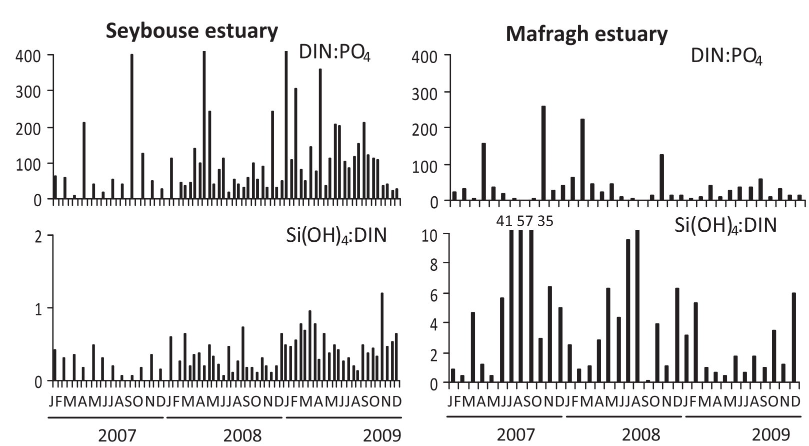

Fig. 5. Variations in $DIN:PO_4$ and $Si(OH)_4:DIN$ ratios in the Seybouse and Mafragh estuaries during the period January 2007–Décember 2009.

Table 1
Nutrient fluxes delivered from the Seybouse and Mafragh estuaries into the Bay of Annaba during the period January 2007 to December 2009.[a]

	Seybouse			Mafragh		
	2007	2008	2009	2007	2008	2009
Precipitation (mm)	650	418	936	730	528	820
Flow ($m^3\ s^{-1}$)		6	37	42	10	35
NH_4 ($t\ yr^{-1}$)		371 (57)	3,510 (543)	235 (73)	25 (8)	160 (50)
NO_2 ($t\ yr^{-1}$)		26 (4)	117 (18)	31(10)	13 (4)	94 (29)
NO_3 ($t\ yr^{-1}$)		102 (16)	512 (79)	228 (71)	70 (22)	207 (65)
DIN ($t\ yr^{-1}$)		500 (77)	4,139 (640)	494 (154)	108 (34)	462 (144)
PO_4 ($t\ yr^{-1}$)		15 (2)	100 (15)	42 (13)	8 (3)	91 (28)
$Si(OH)_4$ ($t\ yr^{-1}$)		353 (55)	4,865 (752)	2,442 (763)	511 (160)	2,259 (706)
DIN:PO_4		55	61	25	31	8
$Si(OH)_4$:DIN		0.63	1.03	17.24	4.14	3.50

[a] Specific fluxes ($t\ km^{-2}\ yr^{-1}$) are given between parentheses. Redfield ratios, annual yield precipitation and average annual flow are also given.

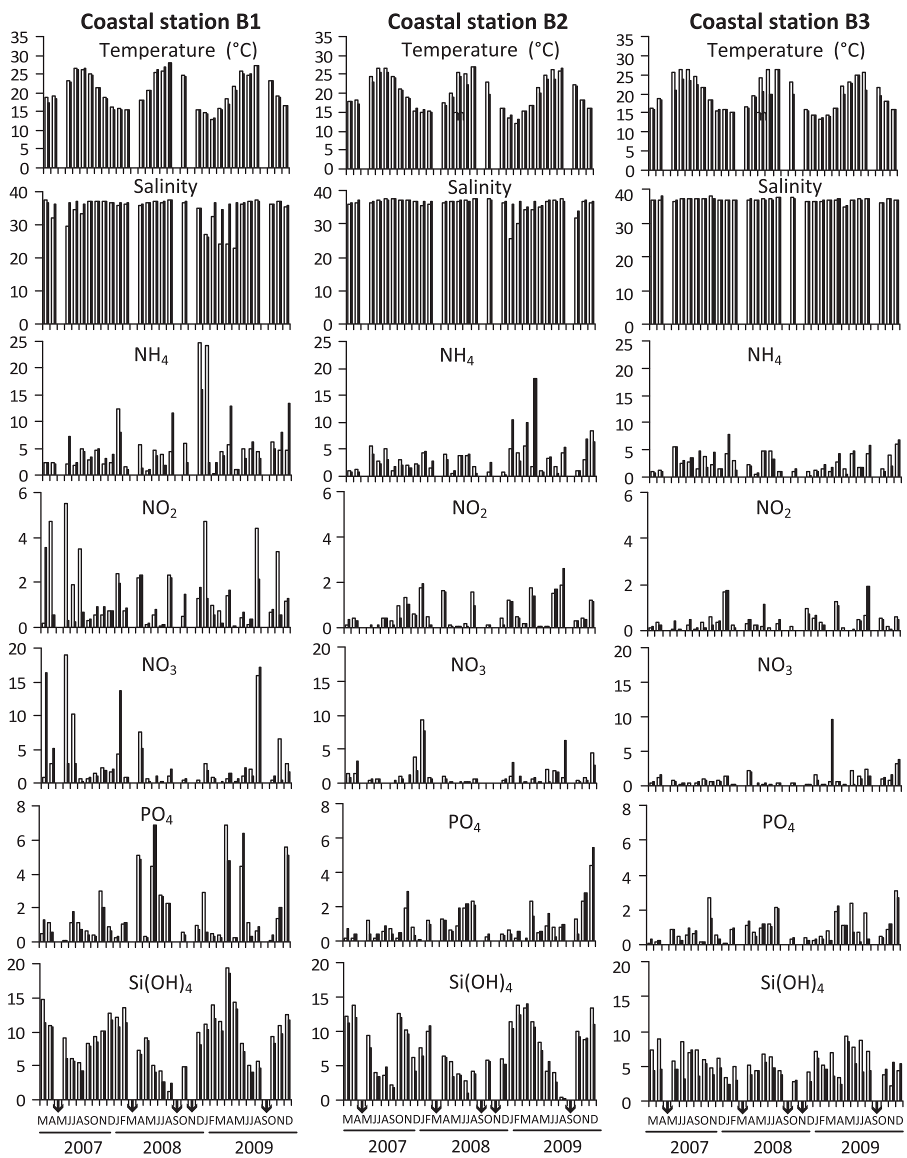

Fig. 6. Seasonal variations in temperature, salinity (pss) and nutrient levels (μM) in the coastal stations (B1; B2; B3) of the Bay of Annaba, March 2007–December 2009. □ Surface; ■ bottom; ↓: not sampled.

stations showed relatively high values at the bottom compared to the surface (Fig. 6).

The average surface levels of PO_4 for the whole area varied from 1 to 1.7 μM, and Seybouse plume station always had the highest value (Fig. 6). The maximum levels rose in the wet period because of continental discharge, and reached 4 μM and 2 μM in the Seybouse and Mafragh plume, respectively. Station B3 which is weakly influenced by continental discharges, had the lowest average values (Fig. 6) throughout the year (0.7–1.2 μM), but high levels could be recorded in winter when river discharge can reach further into the Bay (Fig. 6). As for DIN, the levels of PO_4 at the bottom were comparable to surface values because of winter hydrodynamic mixing. There were however, some perceptible differences between the Mafragh plume and the outer station (Fig. 6).

Similar to the DIN levels, $Si(OH)_4$ at the surface followed a clear spatial distribution with large differences between the station plumes and the outer station (Fig. 6). In the plumes of the estuaries, average surface levels were on the order of 6 μM for the Seybouse and 4 μM for the Mafragh. On the surface of the outer waters at station B3, $Si(OH)_4$ increased to 2 μM but fluctuated greatly throughout the years, between 1 and 9 μM (Fig. 6). The bottom levels were always comparable in the plume stations, but were significantly different from the deeper station in the outer waters.

The Redfield ratios were generally disturbed in all stations in both the surface and bottom waters (Fig. 7). Depending on the station and the year, the DIN:PO_4 ratios were below 10 in 50–70% of samples and the $Si(OH)_4$:DIN ratios were below 1 in 50–70% of samples (Fig. 7). In all stations, the DIN:PO_4 average ratios varied between 2.3 and 11.6, except at the station B1 in 2007 which recorded a ratio of 30. Even though the average values of the $Si(OH)_4$:DIN ratios fluctuated around 1 (0.86–1.6) in all of the stations, they were also imbalanced and below 1 for 50–70% of samples (Fig. 7).

4. Discussion

The objective of this work was to estimate the inorganic nutrient (N, P and Si) fluxes from Seybouse and Mafragh estuaries and to evaluate how much the transfer influenced the distribution of nutrient levels in the Bay of Annaba. Very little is known about the hydrology and chemistry of the Algerian estuaries and their adjacent coasts. Though there is some information about the seasonal nutrient (DIN and PO_4) inputs from the Mafragh estuary (Khélifi-Touhami et al., 2006) and the works of Ounissi and Frehi (1999) and Frehi et al. (2007) describe the DIN and PO_4 observed in the inner part of the Bay of Annaba, information on the Bay hydrology is still lacking.

4.1. The estuaries

The two estuaries introduced large amounts of inorganic nutrients into the Annaba Bay: DIN: 2675; P–PO_4 t yr^{-1}: 105 t yr^{-1} and Si–$Si(OH)_4$: 4347 t yr^{-1}. The Seybouse alone contributed over 80% in of the DIN. For $Si(OH)_4$, the two estuaries supplied comparable fluxes, which originated from land weathering. According to this study, the Seybouse appears to be the major anthropogenic source influencing the chemistry of the Bay of Annaba. In the plume of Seybouse, Frehi et al. (2007) and Ounissi and Frehi (1999) reported very high values in NH_4 (24–40 μM) and PO_4 (2–17 μM). The Seybouse waters were heavily charged with NH_4 throughout the year, with an average as high as 200 μM. The Seybouse waters were strongly dominated by the NH_4 form of reduced nitrogen (80%), which is unusual, compared to the major Mediterranean Rivers where NO_3 dominates. For Mediterranean Rivers, the EEA (2007) reports elevated values of NO_3 ranging from 20 to 376 μM, and in the Ebro River, NH_4 did not exceed 7% of the DIN forms (155 μM) according to Ibáñez et al. (2008). These contrasts may be related to the untreated household wastewaters that are released into the Seybouse river-estuary. Additionally, the high PO_4 levels (4 μM) characterizing the river suggest a strong influence of domestic wastewater. The implementation of European water quality legislation has had a direct impact on the Mediterranean coastal areas. PO_4 levels decreased 6-fold between the late 1980s and 2002 (Torrecilla et al., 2005) for the Ebro River. In addition, the Po River (Cozzi and Giani, 2011), the Rhone River (Diaz et al., 2008), the Têt River (Garcia-Esteves et al., 2007), the Gediz River (Suzal et al., 2008) and several Greek Rivers such as the Pinios (Bellos et al., 2004) and Axios River (Nikolaidis et al., 2009) all saw significant reductions in nutrient loads.

By contrast to the Seybouse estuary, the Mafragh estuary had low levels of all nutrients, and within the nitrogen pool, the NH_4 fraction represented only 30%. However both estuaries seem to be impoverished in $Si(OH)_4$ owing to the estuarine buffering (Canton et al., 2012; Hallas and Huettel, 2013) and to the reservoirs retention (Avilés and Niell, 2007; Humborg et al., 2006; Meybeck and Vörösmarty, 2005) in the upper catchments. Before reaching the coast, riverine nutrients passes through estuaries which act as filters for material derived from land (Canton et al., 2012; Hallas and Huettel, 2013). The disturbance in the quality of water entering the Bay was also expressed in unbalanced Redfield molar ratios. The $Si(OH)_4$:DIN molar ratio for Seybouse waters was low in all seasons, and fluctuated depending on the year from 0.25 to 0.5. In contrast, the Mafragh waters had elevated $Si(OH)_4$:DIN ratios, ranging on average from 2.2 to 13.4. The lesser amount of $Si(OH)_4$ in the Seybouse discharge (73 μM in average) along with the high DIN levels led to the low $Si(OH)_4$:DIN ratio. Even though SiO_4 was also low in the Mafragh estuary, the $Si(OH)_4$:DIN ratio was unbalanced because the anthropogenic inputs was also low. In this case, the Mafragh estuary may be a good example of $Si(OH)_4$:DIN molar ratio trends being controlled by human nitrogen inputs rather than retention in estuaries or reservoirs. Controlling the nitrogen inputs in the catchments therefore seems to be a higher priority than trying to increase Si by lessening dam

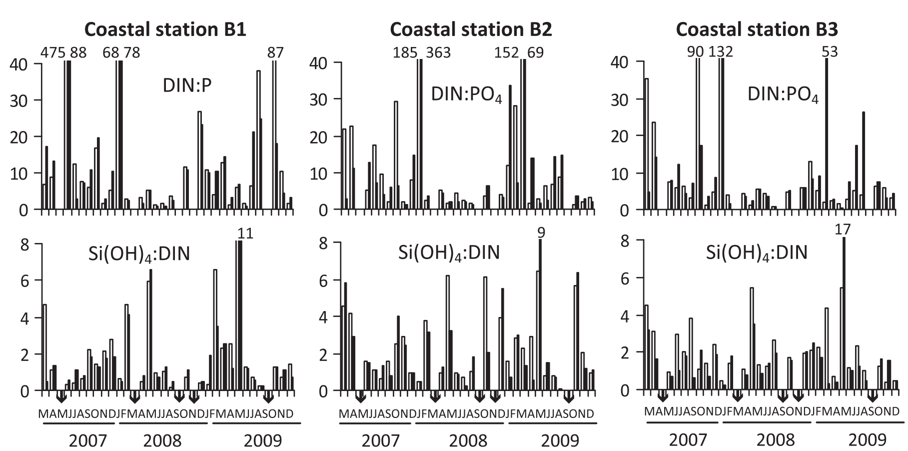

Fig. 7. Variation in DIN:PO_4 and $Si(OH)_4$:DIN ratios in the coastal stations (B1; B2; B3) of the Bay of Annaba during the period March 2007–December 2009. □ Surface; ■ bottom; ↓: not sampled.

construction, in particular for Mediterranean sub-arid regions. As opposed to DIN and PO_4 levels, $Si(OH)_4$ decreases significantly in most Mediterranean (Billen and Garnier, 2007; Ludwig et al., 2009; Ounissi and Bouchareb, 2013) and European Rivers (Conley, 2002; Humborg et al., 2000) owing to the reduction of river discharge and to the retention of dissolved and biogenic silica retention by dams (Conley et al., 2000). Additionally, the $Si(OH)_4$:DIN was always below the phytoplankton requirements in Seybouse waters and about 30% of samples from the Mafragh outlet. Not only did the $Si(OH)_4$ decrease, but the levels of DIN increased under large anthropogenic inputs from the lower Seybouse catchment. The high and balanced $Si(OH)_4$:DIN values in the Mafragh may be related to its large marshland water supply, despite some human population and activity over the catchment. In addition, the NID:PO_4 molar ratio was also unbalanced in all of the Seybouse samples, with average values varying in the range of 90–135 according to the year. The excess of DIN compared to PO_4 seems to indicate an influence of agricultural waste rather than domestic point source inputs. On the other hand, the much higher level of NH_4 compared to NO_3 rather suggests that domestic wastes do impact this estuarine environment. In the Mafragh outlet, the DIN:PO_4 molar ratios were below the phytoplankton needs about half the time, and the annual average values ranged from 24 to 50. Because of the dominance of NO_3 jointly and low levels of PO_4, the Mafragh waters are most likely influenced most by agricultural fertilizers.

The DIN specific loadings from the Seybouse outlet were high, ranging from 77 to 640 kg N km^{-2} yr^{-1} depending on the year. These amounts may be considered among the highest in Mediterranean Rivers (EEA, 2007; Ludwig et al., 2009; Ounissi and Bouchareb, 2013). In contrast to Mafragh outlet where DIN specific loadings were rather low (34–154 kg N km^{-2} yr^{-1} in average), P–PO_4 specific loadings were elevated (3–28 kg P km^{-2} yr^{-1} in average). These masses may also be considered elevated compared to Mediterranean Rivers (e.g., EEA, 1999; Ludwig et al., 2009). Even though levels of PO_4 were important in Seybouse outlet waters, the specific loadings in the catchment were paradoxically low (2–15 kg P km^{-2} yr^{-1}). The low loadings in DIN of Mafragh estuary compared to Seybouse one, is not only because of the smaller human population in the watershed, but may also be linked to the buffering effect of the Mafragh marshland, which provides nutrient sinks. The loadings of Si–$Si(OH)_4$ were remarkably comparable between the two estuaries in both wet and dry years. In addition to the heavy nutrient loads introduced into the Bay, especially via Seybouse, the loading ratios of DIN:PO_4 (>30) and $Si(OH)_4$:DIN (<1), were also unbalanced, suggesting that P and Si may be the limiting factors for coastal phytoplankton growth.

4.2. The bay

The disturbed estuarine inputs have strong effects on impact the adjacent coastal water. The estuary plumes of Seybouse and Mafragh always show high levels compared to the outer waters, where nutrient levels declined 3-fold for DIN and $Si(OH)_4$ and by 2-fold for PO_4. The Seybouse plume was highly enriched by NH_4 (2.8–7 μM) and by PO_4 (1–2.2 μM) throughout the seasons, depending on estuarine inputs. These spatial distributions have also been reported by Frehi et al. (2007) and Ounissi and Frehi (1999).

Compared to the Bay of Annaba, the Bay of Algiers (e.g., Samson-Kechacha, 1981; Bachari Houma, 2009) is less enriched with all nutrients, where NO_3, $Si(OH)_4$ and PO_4 varied respectively in the range of 0.1–5 μM, 0.1–5 μM and 0.05–0.8 μM. At other similar Mediterranean coastal waters, for example the Bay of Tunis, Tunisia (Daly Yahia-Kafi et al., 2005); the Bay of Izmir, Turkey (Kucuksezgin et al., 2006), the Bay of Strymonikos, Greece (Sylaios et al., 2006), the Catalan coastal inner waters, Spain (Flo et al., 2011), the Bay of Annaba show comparable spatial and temporal tendencies of nutrient concentrations. The inner bays directly submitted to continental discharge, are always markedly enriched. However, the outer waters showed different enrichment according to local hydrological conditions. Besides river and domestic wastes input, the Bay of Annaba receives direct industrial wastes (from a great fertilizer factory) highly loaded with NH_4 (200 μM, 1.8 tons day^{-1}) and PO_4 (30 μM, 0.9 ton day^{-1}), which affect the water quality of the receiving coastal water (Ounissi et al., 2008) in particular the N:P ratio. These loadings may represent about 300,000–400,000 inhabitant-equivalent.

These observations confirmed the findings of the correspondence analysis (CA). The factorial plan F1 × F2 of the CA provides 90.2% of the total inertia, where the first factor (F1) contributes 66.2% and the second factor (F2) 24% (Fig. 8). The first factor is mainly explained by the variables NH_4, PO_4 and $Si(OH)_4$:DIN, which are associated with Seybouse and Mafragh estuary observation. The Seybouse discharge was characterized by high level of NH_4 and DIN, as opposed to the Mafragh waters that were richer in $Si(OH)_4$ and NO_3, and with high $Si(OH)_4$:DIN ratios. These two continental nutrient sources also stand in contrast to the DIN:PO_4 ratio, which was lower in Mafragh estuarine inputs. The second factor is explained mainly by the levels of $Si(OH)_4$ and the $Si(OH)_4$: DIN ratio as distributed in the Mafragh estuary and in the Bay. The of Mafragh estuary contributes to explain the F2 because of its high $Si(OH)_4$ levels and $Si(OH)_4$:DIN ratio. These features are opposed to the coastal waters, that are richer in DIN than PO_4 and their DIN:PO_4 ratio is more under the influence of the Seybouse estuary, which is strongly enriched by DIN and NH_4 (Fig. 8). Overall, the first factor may represent the anthropogenic effects from Seybouse estuary with its heavy load of DIN and PO_4 and low $Si(OH)_4$ due to damming, as has been reported in contiguous catchments (Ounissi and Bouchareb, 2013). The second factor may represent the effect of the Mafragh estuary, which seems to play a positive role by

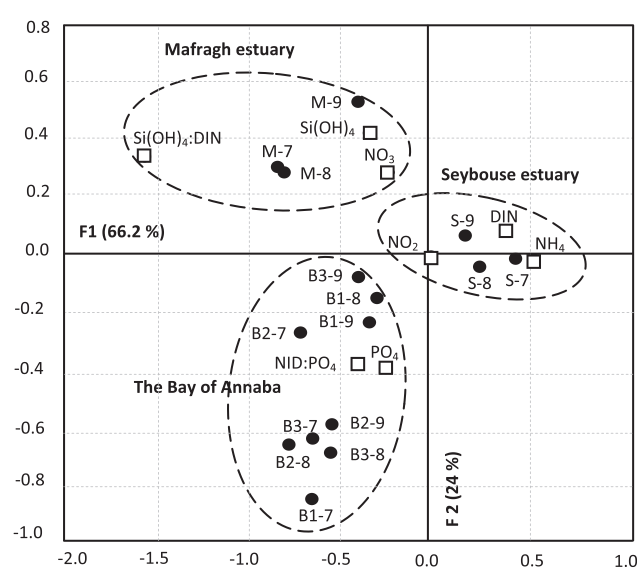

Fig. 8. Factorial plan projection F1 × F2 of the correspondence analysis showing the three segregated areas: F1, the Seybouse estuary with levels of high DIN forms level in contrast to the Mafragh estuary characterized by high levels in SiO_4, NO_3 and elevated SiO_4:DIN ratio; F2, the bay stations both have distinct chemical characters. The variables are NH_4; NO_2; NO_3; DIN; PO_4; $Si(OH)_4$; $Si(OH)_4$:DIN; DIN:PO_4. The objects or sites surveyed in the years 2007; 2008 and 2009 are designated as follow: S-7; S-8; and S-9 for the Seybouse estuary outlet for the years 2007; 2008 and 2009; M-7; M-8; and M-9 for the Mafragh estuary outlet for the years 2007; 2008 and 2009; B1-7; B1-8; B1-9; B2-7; B2-8; B2-9; B3-7; B3-8; and B3-9 for the stations of the Bay. B1, B2 and B3 were surveyed in the years 2007, 2008 and 2009.

enriching the adjacent coastal waters. However, the Seybouse estuary clearly affected the quality of the major contiguous marine waters because of the eastward current (Fig. 1) that brings the water mass to the eastern part of the Bay (Ounissi and Frehi, 1999).

In addition, there was obvious inter-annual variability in nutrient levels as well as seasonal cycles at all spatial scales. These variations in coastal nutrient followed the hydrological cycle of estuarine nutrient and water discharge. The wet years of 2007 and 2009 had more elevated nutrient values and in water discharge while the salinity values decreased significantly according to the freshwater inputs. In the wet years, the Redfield ratios were also more balanced especially for DIN:PO_4 which decreased to 16 and 20 within the estuarine plumes of Seybouse and Mafragh, respectively. These hydrological conditions did not clearly affect the $Si(OH)_4$:DIN ratio, which remained near the standard Redfield ratio value (1:1). This suggests that the continental inputs in the wet periods were more enriched in DIN over $Si(OH)_4$ and that $Si(OH)_4$:DIN increased in the dry years. In the inner Bay, Frehi et al. (2007) and Ounissi and Frehi (1999) reported that the estuarine discharge delivered more DIN than $Si(OH)_4$, which lead to the appearance of harmful species such as *Dinophysis* spp. and *Alexandrium* spp., despite the spring bloom of *Noctiluca miliaris* and other protists such as the *Tintinnids Favella* spp.

Despite the direct anthropogenic influence on river flow, large-scale processes (meteorological pattern, weather patterns, large scale indices) impact the variability of the riverine nutrient discharges and that of the nutrients in the bay. The north Atlantic oscillation (NAO), with centers of action near Iceland and the Azores, has long been identified as an influencing factor on Mediterranean climate variability, especially during winter (Ulbricha et al., 2012). The positive winter NAO is related to below-average precipitation rates over large parts of the western and northern Mediterranean region, with opposite deviations for the negative winter NAO (Trigo et al., 2004, 2006). The Mediterranean atmospheric winter water deficit is positively correlated with the NAO and has been increasing due to the long-term positive anomalies of the NAO since the early 1970s (Mariotti et al., 2002). Links of Mediterranean climate variability to tropical circulation anomalies have been identified. The most important one is the relation to the El Niño Southern Oscillation (ENSO), whose signals from the tropical Pacific area can be propagated downstream as a Rossby-wave train (Alpert et al., 2006), thus affecting regions like the Mediterranean region, far away from the Pacific origin of the dynamical signal. Correlations between ENSO and western Mediterranean rainfall have been found for spring and autumn, but with opposite signs: spring rainfall following ENSO warm events is decreased (Mariotti et al., 2002), whereas autumn rainfall preceding the mature warm phase of ENSO is increased (Mariotti et al., 2005). Over the 50-years period the Mediterranean atmospheric water deficit increased by about 24% in the winter season, and by 9% annually (Mariotti et al., 2002). In contiguous Algerian catchments (Northeastern Algeria), Meddi et al. (2010) reported a decrease of at least 20% of total annual rainfall from the mid-1970s. River discharges with their loads of nutrients into Mediterranean Sea are then doubly affected by the climatic variability and by dams retention. These factors can modulate the eutrophication impact upon these sensitive coastal systems.

5. Conclusions

This work may improve our picture of nutrient inputs into the Mediterranean Sea, because it provides the distribution and nutrient loads of two important Algerian estuaries and their impact on the receiving coastal water quality for the first time. The Seybouse estuary inputs were rich in PO_4 and NH_4 compared to other Mediterranean Rivers, where NO_3 generally dominates. The DIN-specific loadings from the Seybouse outlet may be considered among the highest of Mediterranean Rivers. Both estuaries' outlets were impoverished in $Si(OH)_4$ because of the estuarine buffering and retention by reservoirs. The quality of the water that was introduced into the Bay of Annaba was also reflected in the unbalanced Redfield molar ratios. The $Si(OH)_4$:DIN ratio for Seybouse waters was low in all seasons, rarely exceeding 0.5, in contrast to the Mafragh waters which had consistently balanced $Si(OH)_4$:DIN. The lowering of $Si(OH)_4$ levels in the Mafragh estuary did not affect the $Si(OH)_4$:DIN ratio, which remained almost balanced because DIN inputs were limited in this more pristine watershed. The Mafragh estuary may be a good example of $Si(OH)_4$:DIN molar ratio that is mainly controlled by human nitrogen inputs rather than retention in estuaries or reservoirs. Therefore, controlling nitrogen inputs in catchments seems to be of primary importance compared to lowering by dam construction to allow more Si passage, in particular for Mediterranean sub-arid regions. The Mafragh estuary appears to be less impacted in terms of NH_4 and PO_4; it can play a positive role by introducing clean waters that may mitigate the highly polluted Seybouse inputs. In wet years, the Redfield ratios were more balanced in the inner Bay stations. At the marine stations, because of estuarine inputs, the DIN:PO_4 and $Si(OH)_4$:DIN ratios were below the Redfield standard values in 60% of samples.

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References

Alpert, P., Baldi, M., Ilani, R., Krichak, S., Price, C., Rodó, X., et al., 2006. Relations between climate variability in the Mediterranean region and the tropics: ENSO, South Asian and African monsoons, Hurricanes and Saharan Dust. In: Lionello, P., Malanotte-Rizzoli, P., Boscolo, R. (Eds.), The Mediterranean Climate: An Overview of the Main Characteristics and Issues. Elsevier, Amsterdam, pp. 149–177.

Avilés, A., Niell, F.X., 2007. The control of a small dam in nutrient inputs to a hypertrophic estuary in a Mediterranean climate. Water Air Soil Pollut. 180 (1–4), 97–108.

Bachari Houma, F., 2009. Modélisation et cartographie de la pollution marine et de la bathymétrie (côtes d'Alger) à partir de l'imagerie satellitaire. Thèse de doctorat, Université du Val de Marne Paris XII, Paris, p. 257.

Bellos, D., Sawidis, T., Tsekos, I., 2004. Nutrient chemistry of River Pinios (Thessalia, Greece). Environ. Int. 30, 105–115.

Béthoux, J.P., Morin, P., Ruiz-Pino, D.P., 2002. Temporal trends in nutrient ratios: chemical evidence of Mediterranean ecosystem changes driven by human activity. Deep Sea Res. Part II 49 (11), 2007–2016.

Billen, G., Garnier, J., 2007. River basin nutrient delivery to the coastal sea: assessing its potential to sustain new production of nonsiliceous algae. Mar. Chem. 106, 148–160.

Bosc, E., Bricaud, A., Antoine, D., 2004. Seasonal and inter-annual variability in algal biomass and primary production in the Mediterranean Sea, as derived from 4 years of Sea WiFS observations. Glob. Biogeochem. Cy. 18 (1), <http://dx.doi.org/10.1029/2003GB002034>.

Canton, M., Anschutz, P., Poirier, D., Chassagne, R., Deborde, J., Savoye, N., 2012. The buffering capacity of a small estuary on nutrient fluxes originating from its catchment (Leyre estuary, SW France). Estuar. Coast. Shelf Sci. 99, 171–181.

Cloern, J., 2001. Our evolving conceptual model of the coastal eutrophication problem. Mar. Ecol. Progr. Ser. 210, 223–253.

Conley, D.J., 2002. Terrestrial ecosystems and the global biogeochemical silica cycle. Glob. Biogeochem. Cy. 16 (4), 8, <http://dx.doi.org/10.1029/2002gb001894>.

Conley, D.J., Stalnacke, P., Pitkanen, H., Wilander, A., 2000. The transport and retention of dissolved silicate by rivers in Sweden and Finland. Limnol. Oceanogr. 45 (8), 850–853.

Cozzi, S., Giani, M., 2011. River water and nutrient discharges in the Northern Adriatic Sea: current importance and long term changes. Cont. Shelf Res. 31, 1881–1893.

Daly Yahia-Kafi, O., Souissi, S., Gomez, F., Daly Yahia, M.N., 2005. Spatio-temporal distribution of the dominant Diatom and Dinoflagellate species in the Bay of Tunis (S.W. Mediterranean Sea). Medit. Mar. Sci. 6 (1), 17–34.

Dervin, C., 1988. Comment interpréter les résultats d'une analyse factorielle des correspondances? ITCF-INAPG, Paris.

Diaz, F., Naudin, J.-J., Courties, C., Rimmelin, P., Oriol, L., 2008. Biogeochemical and ecological functioning of the low-salinity water lenses in the region of the Rhone River freshwater influence, NW Mediterranean Sea. Cont. Shelf Res. 28, 1511–1526.

European Environment Agency (EEA), 1999. State and Pressures of the Marine and Coastal Mediterranean Environment. Environmental Assessment Series, vol. 5, Office for Official Publications/EE, L-2985 Luxembourg, p. 137.

European Environment Agency (EEA), 2007. Waterbase, v7. Available from: <http://www.dataservice.eea.europa.eu/dataservice/metadetails.asp?id=984>.

Flo, E., Garcés, E., Manzanera, M., Camp, J., 2011. Coastal inshore waters in the NW Mediterranean: physicochemical and biological characterization and management implications. Estuar. Coast. Shelf Sci. 93, 279–289.

Frehi, H., Couté, A., Mascarell, G., Perrette-Gallet, C., Ayada, M., Kara, M.H., 2007. Dinoflagellés toxiques et/ou responsables de blooms dans la baie d'Annaba (Algérie). C. R. Biologie 330, 615–628.

Garcia-Esteves, J., Ludwig, W., Kerherve, P., Probst, J.-L., Lespinas, F., 2007. Predicting the impact of land use on the major element and nutrient fluxes in coastal Mediterranean Rivers: the case of the Tèt River (Southern France). Appl. Geochem. 22, 230–248.

Hallas, M.K., Huettel, M., 2013. Bar-built estuary as a buffer for riverine silicate discharge to the coastal ocean. Cont. Shelf Res. 55, 76–85.

Howarth, R.W., Marino, R., 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: evolving views over three decades. Limnol. Oceanogr. 51, 364–376.

Humborg, C., Conley, D.J., Rahm, L., Wulff, F., Cociasu, A., Ittekot, V., 2000. Silicon retention in river basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. Ambio 29, 45–51.

Humborg, C., Pastuszak, M., Aigars, J., Siegmund, H., Morth, C.M., Ittekot, V., 2006. Decreased silica land-sea fluxes through damming in the Baltic Sea catchment. Significance of particle trapping and hydrological alterations. Biogeochemistry 77, 265–281.

Ibáñez, C., Prat, N., Duran, C., Pardos, M., Munne, A., Andreu, R., Caiola, N., Cid, N., Hampel, H., Sanchez, R., Trobajo, R., 2008. Changes in dissolved nutrients in the lower Ebro River: causes and consequences. Limnetica 27 (1), 131–142.

Justic, D., Rabalais, N.N., Turner, R.E., 1995. Stoichiometric nutrient balance and origin of coastal eutrophication. Mar. Pollut. Bull. 30, 41–46.

Khélifi-Touhami, M., Ounissi, M., Saker, I., Haridi, A., Djorfi, S., Abdenour, C., 2006. The hydrology of Mafragh estuary (Algeria): transport of inorganic nitrogen and phosphorus to the adjacent coast. J. Food Agric. Environ. 4 (2), 340–346.

Kucuksezgin, F., Kontas, A., Altay, O., Uluturhan, E., Darilmaz, E., 2006. Assessment of marine pollution in Izmir Bay: nutrient, heavy metal and total hydrocarbon concentrations. Environ. Int. 32, 41–51.

Ludwig, W., Dumont, E., Meybeck, M., Heussner, S., 2009. River discharges of water and nutrients to the Mediterranean and Black Sea: major drivers for ecosystem changes during past and future decades. Prog. Oceanogr. 80, 199–217, <http://www.dx.doi.org/10.1016/j.pocean.2009.02.001>.

Mariotti, A., Struglia, M.V., Zeng, N., Lau, K.M., 2002. The hydrological cycle in the Mediterranean region and implications for the water budget of the Mediterranean Sea. J. Climate 15, 1674–1690.

Mariotti, A., Ballabrera-Poy, J., Zeng, N., 2005. Tropical influence on Euro-Asian autumn rainfall variability. Clim. Dyn. 24, 511–521.

Meddi, M.M., Assani, A.A., Meddi, H., 2010. The temporal variability of annual rainfall in the Macta and Tafna catchments, Northwestern Algeria. Water Resour. Manage. 24, 3817–3833, <http://www.dx.doi.org/10.1007/s11269-010-9635-7>.

Meybeck, M., 2003. Global analysis of river systems: from Earth system controls to Anthropocene syndromes. Philos. Trans. Roy. Soc. Lond. B 358, 1935–1955.

Meybeck, M., Vörösmarty, C., 2005. Fluvial filtering of land-to-ocean fluxes: from natural Holocene variations to Anthropocene. C. R. Geoscience 337, 107–123.

Milliman, J.D., 2007. Impact of Human Activities on Present-Day Mediterranean Rivers. Rapp. CIESM, p. 38.

Millot, C., Taupier-Letage, I., 2005. Circulation in the Mediterranean Sea. In: Saliot, A. (Ed.), The Handbook of Environmental Chemistry 5(K). Springer-Verlag, Heidelberg, pp. 29–66.

Nikolaidis, N.P., Karageorgis, A.P., Kapsimalis, V., Drakopoulou, P., Skoulikidis, N., Behrendt, H., Levkov, Z., 2009. Management of nutrient emissions of Axios River catchment: their effect in the coastal zone of Thermaikos Gulf, Greece. Ecol. Model. 220 (3), 383–396.

Ounissi, M., Bouchareb, N., 2013. Nutrient distribution and fluxes from three Mediterranean coastal rivers (NE Algeria) under large damming. C. R. Geoscience 345, 81–92, <http://www.dx.doi.org/10.1016/j.crte.2013.02.002>.

Ounissi, M., Frehi, H., 1999. Variability of microphytoplankton and Tintinnida (ciliated protozoa) in an eutrophic sector of the Annaba Gulf (S.W. Mediterranean). Cah. Biol. Mar. 40 (2), 141–153.

Ounissi, M., Khammar, H., Ziouch, O., Saker, I., Haridi, A., Khelifi-Touhami, M., Abdenour, C., 2008. Apports d'azote et de phosphate au littoral d'Annaba par les effluents urbains, industriels et par la rivière Seybouse (Algérie). In: Chouikhi, A., Zibdah, A., Khalaf, A. (Eds.), International Conference on Rapid Urbanisation and Land Use Conflicts in Coastal Cities, vol. 13. INOC, Izmir, Turkey, pp. 181–186.

Parsons, T.R., Maita, Y., Lalli, C.M., 1989. A Manual of Chemical and Biological Methods for Sea Water Analysis. Pergamon Press, Oxford.

Preston, S.D., Bierman, J.R.V.J., Silliman, S.E., 1989. An evaluation of methods for the estimation of tributary mass loads. Water Resour. Res. 25 (6), 1379–1389.

Samson-Kechacha, F.L., 1981. Variations saisonnières des matières nutritives de la Baie d'Alger: Recherche des Facteurs contrôlant le développement du phytoplancton. Thèse de Doctorat 3e cycle, Université STHB, Alger, p. 98.

Scherrer, B., 1984. Biostatistique. Ed. Boucherville, Gaëtan Morin.

Suzal, A., Bizsel, N., Bizsel, K.C., Husrevoglu, Y.S., 2008. Dissolved nutrient behaviour along the estuarine salinity gradient at the Gediz River Mouth (Aegean Sea, Turkey). Turk. J. Eng. Environ. Sci. 32, 67–84.

Sylaios, G., Koutrakis, E., Kallianiotis, A., 2006. Hydrographic variability, nutrient distribution and water mass dynamics in Strymonikos Gulf (Northern Greece). Cont. Shelf Res. 26, 217–235.

Torrecilla, N.J., Galve, J.P., Zaera, L.G., Retamar, J.F., Alvarez, A.N.A., 2005. Nutrient sources and dynamics in a Mediterranean fluvial regime (Ebro river, NE Spain) and their implications for water management. J. Hydrol. 304, 166–182.

Trigo, R.M., Pozo-Vásquez, D., Osborn, T.J., Castro-Díez, Y., Gámiz-Fortis, S., Esteban-Parra, M.J., 2004. North Atlantic oscillation influence on precipitation, river flow and water resources in the Iberian Peninsula. Int. J. Climatol. 24, 925–944.

Trigo, R.M., Xoplaki, E., Zorita, E., Luterbacher, J., Krichak, S.O., Alpert, P., et al., 2006. Relations between variability in the Mediterranean region and mid-latitude variability. In: Lionello, P., Malanotte-Rizzoli, P., Boscolo, R. (Eds.), The Mediterranean Climate: An overview of the Main Characteristics and Issues. Elsevier, Amsterdam, pp. 179–226.

Turley, C.M., 1999. The changing Mediterranean Sea – a sensitive ecosystem? Progr. Oceanogr. 44, 387–400.

Turner, R.E., Qureshi, N.A., Rabalais, N.N., Dortch, Q., Justic, D., Shaw, R., Cope, J., 1998. Fluctuating silicate:nitrate ratios and coastal plankton food webs. Proc. Natl. Acad. Sci. USA 95, 13048–13051.

Ulbricha, U., Lionello, P., Belušic, D., Jacobeitd, J., Knippertze, P., Kuglitschf, F.G., Leckebuschg, G.C., Luterbacherh, J., Maugerii, M., Maherasj, P., Nissena, K.M., Pavank, V., Pintol, J.G., Saaronim, H., Seubertd, S., Toretih, A., Xoplakif, E., Ziv, B., 2012. 5. Climate of the Mediterranean: synoptic patterns, temperature, precipitation, winds, and their extremes. In: Lionello, P. (Ed.), The Climate of the Mediterranean Region-From the Past to the Future. Elsevier, Oxford, pp. 301–346.