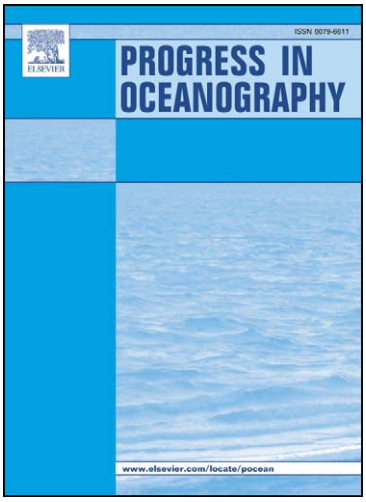
Accepted Manuscript



River discharges of water and nutrients to the Mediterranean and Black Sea: Major drivers for ecosystem changes during past and future decades?

Wolfgang Ludwig, Egon Dumont, Michel Meybeck, Serge Heussner

PII: S0079-6611(09)00002-0
DOI: 10.1016/j.pocean.2009.02.001
Reference: PROOCE 862

To appear in: *Progress in Oceanography*

Received Date: 2 May 2008
Revised Date: 9 February 2009
Accepted Date: 9 February 2009

Please cite this article as: Ludwig, W., Dumont, E., Meybeck, M., Heussner, S., River discharges of water and nutrients to the Mediterranean and Black Sea: Major drivers for ecosystem changes during past and future decades?, *Progress in Oceanography* (2009), doi: 10.1016/j.pocean.2009.02.001

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

ACCEPTED MANUSCRIPT

River discharges of water and nutrients to the Mediterranean and Black Sea: Major drivers for ecosystem changes during past and future decades?

Wolfgang Ludwig [1) *], Egon Dumont [1,3)], Michel Meybeck [2)] and Serge Heussner [1)]

1) Cefrem - Centre de Formation et de Recherche sur l'Environnement Marin (UMR 5110 - CNRS/ Université de Perpignan), Université de Perpignan Via Domitia, 52, avenue Paul Alduy, 66860 Perpignan cedex, France

2) UMR. Sisyphe (CNRS / Université Pierre et Marie Curie) 4, place Jussieu, 75252 Paris Cedex 05, France

3) present address: Centre for Ecology & Hydrology, Maclean Building Benson Lane Crowmarsh Gifford, Wallingford, Oxfordshire, OX10 8BB, United Kingdom

* author for correspondence : ludwig@univ-perp.fr

Abstract

Rivers are important sources of freshwater and nutrients for the Mediterranean and Black Sea. We present a reconstruction of the spatial and temporal variability of these inputs since the early 1960s, based on a review of available data on water discharge, nutrient concentrations and climatic parameters. Our compilation indicates that Mediterranean rivers suffer from a significant reduction in freshwater discharge, contrary to rivers of the Black Sea, which do not have clear discharge trends. We estimate this reduction to be at least about 20% between 1960 and 2000. It mainly reflects recent climate change, and dam construction may have reduced discharge even further. A similar decrease can also be expected for the fluxes of dissolved silica (Si), strongly controlled by water discharge and potentially reduced by river damming as well. This contrasts with the fluxes of nitrogen (N) and phosphorus (P) in Mediterranean and Black Sea rivers, which were strongly enhanced by anthropogenic sources. Their total inputs to the Mediterranean Sea could have increased by a factor of >5. While N still remained at elevated levels in 2000, P only increased up to the 1980 – 1990s, and then rapidly dropped down to about the initial values of the 1960s. With respect to the marine primary production that can be supported by the riverine nutrient inputs, Mediterranean and the Black Sea rivers were mostly phosphorus limited during the study period. Their anthropogenic nutrient enrichment could only have had a fertilizing effect before the general decline of the P loads. When also considering Si as a limiting element, which is the case for siliceous primary producers such as diatoms, silica limitation may have become a widespread phenomenon in the Mediterranean rivers since the early 1980s. For the Black Sea rivers, this already started the late 1960s. Gross primary production sustained by rivers (PPR) represents only less than 2% of the gross production (PP) in the Mediterranean, and less than 5% in the Black Sea. Possible ecological impacts of the changing river inputs should therefore be visible only in productive coastal areas, such as the Gulf of Lions, where PPR can reach more than two thirds of PP. Reported ecosystem changes both in the Adriatic Sea and the Black Sea are concomitant with major changes in the reconstructed river inputs. Further work combining modelling and data collection is needed to test whether this may also have been the case for coastal ecosystems at other places in the Mediterranean and Black Sea.

Keywords: Mediterranean rivers, Black Sea, water discharge, nutrients, climate change, ecosystem response

ACCEPTED MANUSCRIPT

1. Introduction

2. Drainage basins characteristics

3. Water discharge

3.1 Literature estimates
3.2 River discharge trends
3.3 Climate forcing
3.4 Anthropogenic water use
3.5 Large-scale evolution of freshwater budgets
3.6 Hydrological implications

4. Nutrient loads

4.1 Forms and levels of riverine nutrients
4.2 Spatial variability of N and P in rivers
4.3 Temporal variability
4.4 Silica fluxes
4.5 Large-scale evolution of nutrient budgets
4.6 Biological implications

5. Conclusions

6. Acknowledgements

7. References

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

1. Introduction

In 2000 the total population in countries bordering the Mediterranean Sea was about 430 million people and it is expected to reach 520 million by 2025 (Attané and Courbage, 2001). Population densities are greater in the coastal zone than in inland areas. This contrast is particularly strong in the southern countries, where peak values of >20000 inhabitants per km^2 can be found in the upper part of the Nile Delta (PNUE, 2001). Exploitation of the coastal resources represents the major income for people living in the coastal zone, traditionally through fisheries and agriculture, but increasingly also via tourism, as the Mediterranean has become the greatest tourist destination in the world (Turley, 1999). Preservation of the coastal productivity and the ecological health of the marine ecosystems is therefore a first order priority for a stable socio-economic development in this region.

Rivers do play a particular role in sustaining the marine productivity in the Mediterranean Sea. The latter is a semi-enclosed ocean basin and does have a high value of drainage area to surface area compared to the open ocean. The other reason for the strong connection to the river inputs is related to the oligotrophic character of the Mediterranean Sea. Because of its negative water balance and the resulting water circulation, Mediterranean deep waters export great amounts of nutrient to the Atlantic Ocean (Hopkins, 1985), where they are definitively lost for the basin internal primary production. Zones of high productivity are therefore mainly restricted to the coastal waters in the vicinity of major freshwater inputs, as this is shown by satellite images on chlorophyll concentrations in surface waters (e.g. Bosc et al., 2004).

There is strong evidence that the river discharges of water and associated elements to the Mediterranean Sea underwent important changes during recent decades. These changes are probably more important than at most other places in the world due to two main causes. First, water resources in the Mediterranean are scarce and anthropogenic pressures on rivers are particularly important. River damming and water extractions for irrigation and other purposes rapidly evolved since the 1950s (Margat and Treyer, 2004) and profoundly altered the natural functioning of Mediterranean rivers. Second, the Mediterranean region is strongly affected by climate change. Both climate monitoring and modelling studies revealed a general trend toward drier and warmer conditions, which already started in the last century, and which is supposed to worsen even further in the future (Gibelin and Déqué, 2003; Milly et al., 2005; Norrant and Douguédroit, 2005; Christensen et al., 2007; Giorgi and Lionello, 2008). Strong repercussions for riverine water discharges can be expected.

Changes in Mediterranean riverine inputs are therefore potential drivers for long term changes in the marine ecosystems. To verify this, detailed evaluations of the river inputs are needed. We propose in this study a quantitative assessment of the freshwater and associated nutrients fluxes to the Mediterranean by rivers during the last 50 years. The study was initiated on behalf of UNEP – MEDPOL (Ludwig et al., 2003) and completed by further research in order to refine the budgets. We also address the question of the possible impacts on the marine waters, although it is beyond the scope of our work to fully assess the possible ecosystem responses. This requires modelling based on detailed parameterisations of the geophysical, biochemical and ecological properties of the marine system. Our main goal is to highlight the major changes that characterise the Mediterranean rivers, as a guidance for further research directions on the productivity and ecological functioning of the Mediterranean Sea.

ACCEPTED MANUSCRIPT

We focus on the period of 1960 to 2000. Before 1960, river water quality monitoring programs were not established and time series on nutrients and other elements were insufficient for accurately assessing nutrient discharges. Moreover, since the sixties, large-scale monitoring and scientific cruises on the biogeochemistry and biology of the Mediterranean surface and deep waters started to be more frequent, and possible changes can be compared to changes in the riverine nutrient supply. Finally, this period is interesting with respect to the influence of climate change. It covers the strong temperature increase which has been recorded since the second half of the 1970s in many parts of the northern hemisphere (Trenbert et al., 2007).

Although we are mainly concerned with the Mediterranean system, we include in our review also the rivers of the Black Sea. The Black Sea has a positive water balance and delivers mesohaline water to the Mediterranean Sea through the Dardanelles straight. Consequently, changes in river inputs to the Black Sea will also affect the Mediterranean ecosystem. But this comparison is also interesting for other reasons. Climatic and hydrodynamic conditions of the Black Sea drainage basin are very different from the Mediterranean Sea and comparing these semi-enclosed seas emphasizes the peculiarities of the Mediterranean water cycle.

2. Drainage basins characteristics

The Mediterranean Sea covers about 2.5 million km^2, with an average water depth of about 1.5 km. It is commonly divided in ten sub-basins (Cruzado, 1985), which are shown in Figure 1 and characterized in Table 1. The drainage basin of the Mediterranean stretches over more than 5 million km^2. This value also includes the Nile (South-Levantine Basin) and the hinterlands of the Libyan coast (Central Basin), which are not active parts of the drainage basin. By far most of the water discharge of the Nile is lost through evaporation, now strongly increased by an intensified agricultural water use after the construction of the Aswan High Dam. The drainage basin of the Central Sea is mostly desert with a badly organized hydrological network that only becomes active when climate switches to more humid conditions (Vörösmarty et al., 2000a).

Without these extensive areas that have a relatively small riverine input, the drainage basin of the Mediterranean Sea reduces to less than 1.5 million km^2 and the average land to sea area ratio is 0.55 (0.79 for the Western and 0.43 for the Eastern basin). This contrasts strongly with the Black Sea, where this ratio is almost ten times greater (see Table 1). Given the potential impact of riverine nutrients on primary production in the sea, it is therefore not surprising that biological productivity in the Black Sea is on average more elevated than in the Mediterranean (see section 4.6 below for literature estimates), even if the very different hydrodynamic functioning of both seas makes a direct comparison difficult. Also the productivity differences among the Mediterranean sub-basins can be better understood on the basis of this ratio. Notice that the highest value is obtained for the Adriatic Sea, where annual primary production rates are the highest of the Mediterranean (Bosc et al., 2004).

Climatically, the Mediterranean is characterised by warm temperatures, winter-dominated rainfall, dry summers and a profusion of microclimates due to local environmental conditions (Ludwig et al., 2003). Mean annual temperature follows a marked north to south gradient to which local orographic effects are superimposed. Lowest average temperatures of <5 °C are found in the higher parts of the Alps,

ACCEPTED MANUSCRIPT

whereas temperatures of >20 °C are typical for Libya and Egypt. Mean annual precipitation has a general decreasing north-to-south gradient with orography as a naturally modulating factor. Annual precipitation values of 1500-2000 mm yr^{-1} and more exist in the alpine and Pyrenean headwater regions of the Po, the Rhone and the Ebro rivers, and are very common in the alpine mountain belt bordering the Dalmatian coast, from the Istrian peninsula down to Albania. This region is the wettest region in the Mediterranean area.

The strong summer-winter rainfall contrast is the major characteristic of the Mediterranean climate. This contrast increases from north to south and from west to east (Ludwig et al., 2003). Precipitation mainly occurs during winter and autumn, and often less than 10% of the annual precipitation falls during summer. This contrasts strongly with the continental climate in the drainage basin of the Black Sea, where most precipitation occurs during summer (except the Turkish part). High precipitation during autumn is typical for the coasts of Spain, France, Italy, Croatia, Yugoslavia, Albania and Greece. Further east, such as in Turkey and Lebanon, autumn precipitation is less important and by far most precipitation occurs in winter.

When ranking according to annual water discharge, the ten largest rivers of the Mediterranean Sea are the Rhone, Po, Drin-Buna, Nile, Neretva, Ebro, Tiber, Adige Seyhan and Ceyhan rivers. Together they account for about half of the average freshwater input by rivers. The Rhone and the Po alone account for about one third (see also below). The ten largest rivers of the Black Sea (including the Sea of Azov) are the Danube, Dnieper, Don, Rioni, Kuban, Dniester, Coruh, Kizil Irmak, Sakarya, and Yesil Irmak rivers, carrying about 85% of the riverine freshwater to the Sea (Jaoshvili, 2002; Algan, 2006). The Danube alone brings along about half of the water. The rest of the rivers are small and assembling them to complete the freshwater and nutrient budgets is almost impossible. This is particularly true for the Mediterranean basin that has a great number of very small rivers (Milliman, 2001), due to strong relief favouring the formation of small watersheds.

3. Water discharge

Water discharge is the main factor controlling matter transfer from land to sea by rivers. Even if the concentrations of different elements are estimated precisely, flux estimates can only be as reliable as the estimates for the corresponding water discharge. Consequently, constituent fluxes mainly depend on the hydrological conditions. We therefore start our review with an assessment of the riverine freshwater inputs to the Mediterranean and Black Sea. Freshwater inputs alone can influence the marine ecosystems functioning through their control on the general water circulation in the Mediterranean Sea (e.g. Skliris et al., 2007).

3.1 Literature estimates

Estimates of total riverine freshwater flux into the Mediterranean and Black Sea have been established through inventories of major rivers (UNEP, 1978; Jaoshvilli, 2002), mapping of average runoff depths (Korzoun et al., 1977), modelling (e.g. Vörösmarty et al., 1998) or country-based inventories of water resources (Margat and Treyer, 2004). Most of them vary around 400-450 km^3 yr^{-1} and 350-400 km^3 yr^{-1} for the Mediterranean and Black Sea, respectively (Table 2). Major differences between these estimates arise because of the Nile basin, which alone is a water resource of > 200 km^3 yr^{-1}, but which looses most of its water through infiltration in

ACCEPTED MANUSCRIPT

swamps, river evaporation and anthropogenic water use (Nixon, 2003). These processes cannot be taken into account by classical mapping and modelling approaches, leading sometimes to a tremendous overestimation of the freshwater fluxes to the South Levantine Sea. The construction of the Aswan High Dam in 1965 had a major impact on the water discharge, and the Nile River now only brings about 6 (Abu El Ella, 1993) to 15 (Nixon, 2003) km^3 yr^{-1} to the Mediterranean. However, previous studies sometimes exaggerated the effect of the dam construction (e.g. Skliris et al., 2007), since they compared this present-day value with the natural long-term discharge at Aswan (about 83 km^3 yr^{-1}). The water is here still far away from the sea and anthropogenic water use in the lower Nile has a long history. The pre-damming value at the river mouth was probably only slightly more than half of the discharge at Aswan (Nixon, 2003).

3.2 River discharge trends

The detection of trends requires the availability of long term time series of river discharge. Unfortunately, the release of hydrological data from national monitoring networks is not as common as for climate data. This is particularly true in the Mediterranean context, where water resources represent an important economical value and political barriers probably still inhibit more transparency on river data.

For our purpose, we could assemble time series of 37 Mediterranean and Black Sea rivers (Table 3), given the condition that they should cover at least 20 years within our period of interest. Many of the records were downloaded from the Medhycos data server (Medhycos, 2001), which probably included the most complete compilation of hydrological data in the Mediterranean region. Other time series were taken from the Global River Discharge database RivDIS (Vörösmarty et al., 1998), or were obtained from the Hydro database hosted at the French Ministry of Environment (Hydro, 2006). The spatial distribution of the rivers covers the entire Mediterranean and Black Sea drainage basin, although certain regions are not well represented. In general, data coverage of the north-European rivers is good, whereas data on south-Mediterranean rivers are less abundant. Turkish rivers are missing in our data. The succession of dry and wet periods is normally well correlated for rivers of the same regions, indicating that the records are representative.

We performed trend analyses for all records on the basis of the Mann-Kendall test (Mann, 1945; Kendall, 1975). If significant trends were detected, we determined the long-term discharge change via calculation of the Sen slope estimator (Sen, 1968). Negative values indicate significant discharge decreases. Comparison of trends between rivers (Table 3) has to be done with caution because their time series do not necessarily cover the same periods. Moreover, size differences can reduce the comparability, since small basins may be much more subjected to local patterns. Another problem is that some time series have gaps which, because of the rhythmic succession of dry and humid periods that exist in the Mediterranean drainage basin (e.g. the 20 year cycles described by Zanchettin et al. (2008) for the Po River), can influence the trend results. Also, the gauging stations are not always situated close to the river mouth and only reflect a certain portion of total discharge. Despite these limitations, we consider that the available data still allow a good overview of the general evolution of Mediterranean river discharges.

The results of the trend analyses reveal strong negative trends for half to two third of the Mediterranean rivers, depending on the chosen confidence level. For the other rivers, no significant trends could be detected. But these records often stop in the

ACCEPTED MANUSCRIPT

1980s which began with high precipitation (see below), and the trends may be overwhelmed by the general periodicity of dry and wet periods. Strongest negative trends appear for rivers that were affected by the construction of dams, such as the Ebro River in Spain and the Moulouya River in Morocco. The strongest decrease is found for the Cetina River in Croatia where large artificial reservoirs (Peruca and Busko Blato) have been built for hydropower, water supply and flood protection. Discharge reductions are frequent in the rivers of the eastern Mediterranean when the records extend to recent years rather than stopping in the eighties. This is in agreement with Skoulidikis and Gritzalis (1998) who reported that many Greek rivers reduced to up to half of their original discharge

The Po and the Rhone rivers, which are the greatest rivers of the Mediterranean in terms of their freshwater fluxes, do not follow the general trend. Their water discharge remains about constant. This remains true when looking at longer time spans (Zanchettin et al., 2008), contrary to most Mediterranean rivers for which long term records exist (Ludwig et al., 2003). Like most Mediterranean rivers, these two large rivers were affected by impoundments and dam constructions. Their outstanding behaviour may be explained by the non-Mediterranean climate in the upper northern parts of their basins.

The rivers of the Black Sea do not show clear trends during the considered period (Table 3). The Danube and the Dniepr are the only rivers where the records extend to recent years, whereas the other records stop already in 1984. This complicates the detection of long term trends. Nevertheless, it seems that the general trend towards decreasing water discharge of the Mediterranean rivers is absent in the Black Sea. Only for the Kuban River, a decreasing tendency is indicated, probably in relation with the construction of its major dam in 1975 (Krasnodar dam). Also many of the other Black Sea rivers have been affected by dam constructions, but mostly before 1960 (Tolmazin, 1985).

3.3 Climate forcing

The patchiness of the discharge records makes it difficult to extrapolate the detected changes to larger spatial and temporal scales unless the records are compared to the general evolution of climate. The Climatic Research Unit of the University of East Anglia (Norwich, UK) produced spatially gridded time series of precipitation and temperature data which entirely cover the years 1960-2000 (Mitchell and Jones, 2005). These data can be compared with the discharge records. When averaging the climatic parameters over the different Mediterranean and Black Sea drainage basins (Fig. 1), and submitting them to trend analyses in the same way as the river discharge records, it becomes evident that climate in the Mediterranean clearly evolved towards dryer conditions (Table 4 and Fig. 2). Both for drainage basins of the Western and Eastern Mediterranean Sea, there is a highly significant negative trend for precipitation, indicating that the averages decreased by about 11% in both. In the western basin, the decrease is particularly important for the Alboran Sea (-34%). Also the Southwestern Sea seems to be affected by a precipitation decrease. In the eastern basin, reductions are found for the Aegean Sea (-13%), the South-Levantine Sea (-10%), and, although with a lower significance level, also for the Adriatic Sea. Our estimate of a 62 mm reduction over the total Mediterranean drainage basin in Table 4 is in general agreement with the study of Xoplaki et al. (2004), who reported a general precipitation decrease of -2.2 mm month^{-1} decade^{-1} for the wet season over this area (October to March) since 1950. Applied to our study period, this corresponds to a total reduction of 54 mm.

ACCEPTED MANUSCRIPT

Temperature, on the other hand, strongly increased. The only exceptions are the drainage basins of the Ionian, Aegean and North-Levantine seas, where the trends are statistically not significant. When neglecting the very dry basin parts in the south (SLE and CEN), the temperature increase is on average more important in the Western Mediterranean than in the Eastern basin, with a "hot-spot" in the Northwestern Sea, where the average temperature increase was greatest (+1.3 °C). Higher temperatures can increase evapotranspiration in the drainage basins, and therefore decrease water discharge too. Lespinas (2008) reported an average temperature increase of about 1.5 °C for the period 1965 – 2004 in a regional study on the coastal river basins in the Gulf of Lions. Although annual precipitation remained approximately constant, they showed that water discharge decreased in this region, mainly by a temperature related reduction of the basin internal water storage in the snow, soil and groundwater reservoirs.

Quantification of the combined effect of decreasing precipitation and increasing temperatures on the freshwater discharge to the Mediterranean Sea can be estimated by following the approach of Pike (1964). He proposed to calculate the mean annual runoff ratio (RR = runoff/ precipitation) as a function of the ratio of the mean annual precipitation total (APPT) over the mean annual potential evapotranspiration (APE):

$$RR = 1 - 1/[1+(APPT/APE)^2]^{0.5} \qquad \text{(i)}$$

According to Holdridge (1959), APE can be derived in a first order approximation as a linear function of the mean annual biotemperature (ABT; APE = ABT * 58.93), which is the average of all monthly temperatures for which negative values were set to zero. A theoretical runoff (Q-Pike) can consequently be obtained by multiplication of RR and APPT.

Our data indicate that this approach is a valuable predictor of runoff in Mediterranean river basins. For the Rhone and Po rivers, it reproduces the observed runoff depths (Q) errors of less than 15% (Fig. 3a,b), and the inter-annual variations during 1960-2000 are similar. Also for the other Mediterranean rivers in Table 3 for which we could easily identify their drainage basins in our simplified hydrological network (Fig. 1), Q-Pike gives reasonable estimates of the observed Q values, with no systematic bias (over- or underestimation). Underestimations are slightly more frequent than overestimations (not shown), but this relates to the fact that some of the monitoring stations in Table 3 are far upstream where average runoff depth are normally higher than near the river mouths

For the Black Sea rivers, Q-Pike can overestimate Q, particularly the case in the western (e.g. Danube – Fig. 3d) and northern part of the drainage basin, where overestimations can reach 50-100%. Here, climate is characterized by a continental precipitation regime, and summer precipitation can even exceed precipitation in winter (Ludwig et al., 2003). This sharply contrasts with the Mediterranean climate. Precipitation during the warm seasons is less efficient for the generation of runoff than precipitation during the cold seasons because of the greater evapotranspiration potential. This can explain the overestimated Q. Interestingly, the Adige is the only Mediterranean river in our data set for which Q-Pike has an important overestimation too. Seasonality of water discharge of this river is very untypical for the Mediterranean climate, with low values in winter and high values in early summer (Ludwig et al., 2003).

ACCEPTED MANUSCRIPT

But at least for the Mediterranean, Q-Pike allows a realistic evaluation of the impact of climate forcing on the river freshwater fluxes to the sea. Application of this model to the entire drainage basin indicates that climate change alone could have provoked a water discharge reduction of more than 20% (Table 4). Strongest reductions appear for the Alboran (-64%), Southwestern (-31%), Southern-Levantine (-25%), Aegean (-24%) and Adriatic (-17%) seas. For the Black Sea, the Q-Pike derived estimates may be somewhat too high, but it can be assumed that the inter-annual variability are correctly reproduced. As both the evolutions of precipitation and temperature were stationary (Fig. 2 and Table 4), no clear trends can be detected in estimated water discharge. This is in good agreement with the absence of trends in the discharge records of the Black Sea rivers (see section 3.2)

3.4 Anthropogenic water use

Also reservoirs can reduce the natural water discharge of rivers, in particular when they allow water extraction for irrigation of the fields. The Ebro River in Spain is a typical example where damming was continuously developed for agricultural purposes. This river counts nowadays about 128 dams in its basin (Ibanez et al., 1996) and the strong and continuous reduction of its water discharge (see Table 3) is commonly attributed to anthropogenic water use. However, climate evolved towards dryer conditions too. Extracting the average Q-Pike values for this basin, and submitting them to trend analyses for the same period as for which the observed Q exist, results in a decrease of about 36%, compared to the 64% decrease of the observed Q. This indicates that more than half of the reduction was related to climate change, and the rest to anthropogenic water extraction (see also Fig. 3c).

Another interesting example is the Moulouya River in the drainage basin of the Alboran Sea. Here, climate induced water stress was greatest in the Mediterranean region (see above) and a major dam (Mohamed V) was constructed in 1967 (Snoussi et al., 2002). The predicted runoff decrease of this river (-72%) is almost fully reproduced by trend analyses of the Q-Pike predictor (-69%). However, when discharge records show major breaks in relation to dam constructions, trend analyses are probably not appropriate, since the records do not necessarily follow continuous changes before and after the breaks. Comparing Q-Pike and observed discharge before and after the dam construction suggests that water extraction may have reduced the river discharge by about 20%.

Finally, we also tested an example of a river basin under more humid climate conditions. The Krka River is particularly interesting because its basin is situated in a natural park and free of major anthropogenic impacts (Kniewald et. al., 2006). Also here, the negative trend of this river in Table 3 (-29%) is close to the trend in the corresponding Q-Pike values (-25%).

The above discussed rivers are only examples. The climatic data we used were produced in a coarse resolution and trend analyses based on these data have to be considered with caution. Nevertheless, our results indicate that climate change is responsible for most of the observed discharge reductions in Mediterranean rivers. Damming and subsequent water extractions can be superimposed and enhance the decline of the water resources, but this is not the main reason for the decrease of river freshwater discharge to the Mediterranean Sea.

3.5 Large-scale evolution of freshwater budgets

ACCEPTED MANUSCRIPT

Table 2 includes our best estimates for the 1960 – 2000 evolution of the freshwater fluxes to the Mediterranean and Black Sea. They were mainly based on the evolutions of the Q-Pike predictor, but wherever we had complete discharge records for major Mediterranean rivers (Rhône, Po, Ebro), we replaced the modelled data by observed ones. For the Nile, we followed the estimates of Nixon (2003) for the average discharge before and after the damming (43 km^3 yr^{-1} and 15 km^3 yr^{-1}, respectively), but varied them proportionally to the variations of Q-Pike in both periods. Also for the Black Sea rivers, we considered the observed discharges when we had complete records (Danube), or completed the missing data according to the average Q-observed/ Q-Pike ratios for the other major rivers (Dniepr, Don, Dniestr, Kuban, Southern Bug, Rioni). The water fluxes we obtained can be compared with the study of Boukthir and Barnier (2000) who established a riverine freshwater budget for the entire Mediterranean for the period 1974-1994. They propose an average value of 350 km^3 yr^{-1}, which is close to the 333 km^3 yr^{-1} we find with our data for the same period.

During the 41 years of interest, the riverine water inputs to the Mediterranean Sea were reduced by about 15-22%, depending on whether this decrease was calculated by projection of the trend analyses (-22%), or by comparison of the average water fluxes during the 1960s and 1990s (-15%). Precise quantification of the reduction is complicated by the fact that the evolution is also superimposed by the cyclicity of humid and dry periods. Long-term series of precipitation and discharge (e.g. in the Rhone and Po rivers) show that in the northern part of the Mediterranean, this cyclicity occurs in intervals of about 20 years (Ludwig et al., 2003; Zanchettin et al., 2008). The period we considered started and ended with relative humid years, which are therefore overrepresented in the 1960s and 1990s averages. This gives some advantage to the results based on the trend projection. Moreover, our approach does not account for additional reductions in many smaller rivers related to damming and anthropogenic water extractions. A decrease of the total freshwater discharge of 80-100 km^3 yr^{-1} by rivers is therefore a realistic estimate for the last 40-50 years. This is close to the combined discharges of the Rhone and Po rivers (about 105 km^3 yr^{-1}). As both rivers did not significantly change their water inputs, these two rivers alone bring nowadays more than one third of the total riverine freshwater to the Mediterranean Sea. Fifty years ago, this was only slightly more than one fourth.

3.6 Hydrological implications

Two of the Mediterranean sub-basins with strong freshwater reductions correspond to basins where deep water formation occurs. These are the Adriatic and Aegean Sea. Deep water formation in the Aegean Sea was only active in the late 1980s and early 1990s when it temporarily replaced the deep water formation in the Adriatic, commonly known as the Eastern Mediterranean Transient (Lascaratos et al., 1999). Our data show that during 1985-1994 the river discharges to the Aegean Sea were suddenly reduced by more than 30% compared to the previous years (1960-1984). This may have contributed to higher salinities in the surface waters, favouring the formation of deep waters.

Skliris et al. (2007) demonstrated by modelling that reductions in the riverine freshwater inputs can cause greater deep water formation rates in the Mediterranean Sea. The authors focussed on the freshwater reductions due to the damming of the Nile and Ebro rivers, summing up to more than 100 km^3 yr^{-1} in their study, which exceeds by far our estimates for these two rivers, but which is close to what we estimate for the entire Mediterranean. These reductions were

ACCEPTED MANUSCRIPT

considered as single events after which the system regains new equilibrium conditions. However, if they were mainly related to climate change, as our data suggest, modifications of the circulation patters can hold on in the future. On the other hand, Somot et al. (2006) showed in a transient climate change simulation that increasing surface salinities related to lower river runoff can be counteracted by thermal induced lowering of the surface densities, which, in combination, could even provoke a decrease of the deep water formation rates towards the end of the 21th century. Further research is therefore needed to understand the impact of riverine freshwater discharges on the circulation patterns in the Mediterranean Sea.

4. Nutrient loads

A reduction of the river freshwater discharge implies a reduction of the associated fluxes of many elements, in particular when they stem from natural sources such as erosion. For nitrogen (N) and phosphorus (P), however, additional inputs from human activities often dominate the natural sources and it has been postulated that between 1970 and 1990, humans increased the global delivery of dissolved inorganic N and P to the oceans by a factor three (Smith et al., 2003; Smith et al., 2005). This could be particularly important for an oligotrophic system like the Mediterranean Sea. Increasing nitrate and phosphate concentrations in the Mediterranean deep waters were considered as indicators of a strong nutrient increase from anthropogenic origins (Béthoux et al., 1998), but testing of this hypothesis was not yet possible because of the lack of precise data on the spatial and temporal variability of riverine nutrient loads.

4.1 Forms and levels of riverine nutrients

The most important macro-nutrients for the marine ecosystem are nitrogen (N), phosphorus (P), and silica (Si). They exist in rivers in various dissolved, particulate, organic and inorganic forms. From a global perspective (e.g., Meybeck, 1982; Foellmi, 1996; Seitzinger et al., 2005), particulate organic nitrogen (PON) is the dominant nitrogen form, even if dissolved inorganic nitrogen (DIN) becomes increasingly important due to a growing anthropogenic contribution (see below). It probably now exceeds PON in the global budgets (Seitzinger et al., 2005). Rocks do not contain N-bearing minerals and PON is absent in rivers, although some DIN can be absorbed on particles (mainly ammonia). Particulate inorganic phosphorus (PIP) is by far the dominant transport form for phosphorus. But unlike nitrogen compounds, dissolved inorganic phosphorus (DIP) can be bound to suspended or settled material, making it difficult to distinguish between dissolved and particulate forms. The P content of rivers may thus be governed by a 'spiral pattern' (Newbold et al., 1981; Amoros and Petts, 1993) involving the sediment phase to which dissolved phosphorus is absorbed and released from. Silica finally is largely transported in the dissolved form. River suspended sediments contain great amounts of silicate minerals but they are insoluble and not available for biological production. Only a small part of the particles contain soluble forms (biogenic particulate silica), contributing to about 10-20% of the total silica flux (Conley, 1997; Conley and Schelske, 2001; Garnier et al., 2002b; Sferratore et al., 2006).

The above-given considerations are based on global averages that do not take into account the great spatial variability on earth, as well as the dynamic evolution of the fluxes during recent years. The budgets for the particulate nutrient forms are dominated by a few high turbid rivers, such as the Asian rivers draining the

ACCEPTED MANUSCRIPT

Himalayan region, while the dissolved forms are strongly influenced by the large tropical rivers, almost free of major anthropogenic impacts. When considering the proportions of specific nutrient forms in more densely populated regions, such as the Mediterranean, the dissolved forms are clearly more important as expected from the global budgets (Table 5). In the case of nitrogen, nitrate is by far the dominant form in the total nitrogen (TN) fluxes. The other DIN species (NO_2^- and NH_4^+) are only abundant when rivers suffer from organic pollution, reducing the oxygen levels, hence allowing the reduced forms to be stable. Thus, monitoring of nitrate is normally sufficient for an assessment of nitrogen enrichment in rivers.

For phosphorus, however, the particulate forms cannot be neglected (Table 5) and monitoring programs often also determine the total phosphorus (TP = sum of all dissolved and particulate P species) content in rivers. But TP concentrations can be strongly linked to the concentrations of total suspended solids (TSS), making it difficult to monitor this parameter accurately. The reason is that the sampling frequency in most monitoring programs is too low to determine reliable average TSS concentrations. This needs to be kept in mind when considering the temporal and spatial variability of average TP levels in rivers. Phosphate levels are less variable and, although phosphate is not necessarily the dominant P form, average values might be more suitable for an assessment of phosphorus enrichment in rivers.

For these reasons, and because of the greater availability of data on nitrate and phosphate compared to the other nutrient forms, we focus hereafter mainly on these two parameters. For conversion to TN and TP, we propose that the average proportions in Table 5 may be considered as representative: $N\text{-}NO_3$/ TN = 0.75 and $P\text{-}PO_4$/ TP = 0.48. These ratios are in good agreement with the study of Turner et al. (2003) who estimated them on the basis of a great number of American and major world rivers to very similar values (0.77 for $N\text{-}NO_3$/ TN and 0.46 – 0.70 for $P\text{-}PO_4$/ TP). The values in Table 5 refer to Mediterranean rivers only, but they seem also to be representative for the Black Sea rivers. According to Behrendt et al. (2005) and Cociasu et al. (1996), $N\text{-}NO_3$/ TN and $P\text{-}PO_4$/ TP in the Danube can be estimated to 0.77 and 0.61, respectively.

4.2 Spatial variability of N and P in rivers

Monitoring of water quality parameters in rivers has been developed at national levels in many riparian countries of the Mediterranean Sea and the Black Sea, but only for recent years these data became widely available. For European rivers, many of them are now centralised in the *Waterbase* database at the European Environmental Agency (EEA, 2007), allowing the nitrate and phosphate levels in western European countries to be quantified (Table 6). Many eastern countries, such as Turkey, as well as African countries are missing however, which can bias the general picture.

For nitrate, Table 6 shows relative moderate specific fluxes in the listed river basins, indicating that nitrogen pollution is not a major problem in Mediterranean rivers. The latter is usually dominated by diffuse sources, in particular agriculture, which is characterized in southern Europe by less intensive cultivation practices. Here, nutrient application to agricultural land (inorganic fertiliser and manure) varied in 1991 only between 30-70 kg N ha^{-1}, compared to 180 kg N ha^{-1} in the Netherlands (Crouzet et al., 1999). Greatest application rates are found in the northern Mediterranean drainage basins, such as those of the Adriatic and North-Western Sea (Fig. 4). As a consequence, high specific NO_3 fluxes are typical for north-Italian rivers. In particular in the Po River plain, agricultural land use is densely

ACCEPTED MANUSCRIPT

developed, and this river has one of the greatest specific nitrate fluxes in Table 6. But it is still low compared to what is commonly reported for the large European rivers further to the north, such as the Seine and Rhine rivers (Billen and Garnier, 2007).

The specific phosphate fluxes in Table 6 are as variable as specific nitrate fluxes. No clear regional pattern can be observed. Phosphorus pollution is normally dominated by point sources, such as urban waste waters. The north to south decreasing trend that is typical for nitrate in Europe is overprinted for phosphate by an upstream to downstream increase (Crouzet et al., 1999), following the distribution of population densities. Greek rivers seem to have particularly elevated phosphate fluxes in Table 6, pointing to greater pollution levels than in other Mediterranean countries. This should be taken with caution, however, as it could be an artefact related to different measurement techniques in the Greek monitoring program. Phosphate levels reported in scientific studies are often clearly lower. A good example is the Pinios River, for which Bellos et al. (2004) found an average $P\text{-}PO_4$ value of 0.075 mg l^{-1} (monitoring in 1996-1998 at the river mouth), almost 10 times lower as the value in Table 6. Notice that the median molar $N\text{-}NO_3$/ $P\text{-}PO_4$ ratio of all listed rivers is about 55. Without Greek rivers it is about 80.

4.3 Temporal variability

Before 2000, data on nitrate and phosphate fluxes in Mediterranean and Black Sea rivers were scarce. Observations mostly refer to scientific studies that were limited in time (Ludwig et al., 2003), making it difficult to catch the long term evolutions. Only the large rivers (Rhone, Po, Ebro, Danube) received more attention because of their importance for the geochemical budgets at larger scales, and more or less complete reconstructions of their nitrate and phosphate fluxes during the last 40 years can be found (Fig. 5a-c). These large rivers have also the advantage that their basins integrate the variety of human activities at regional scales, making them more representative for the general evolutions than smaller river basins.

Nitrate fluxes in the Rhone, Po and Ebro rivers increased steadily from the beginning of the 1970s up to the 1990s, before they remained approximately constant, or even decreased during recent years. The early increases were greater in the Ebro and Po rivers than in the Rhone River. On the basis of the Sen slope estimator (see above), it can be estimated that for the 1970-1995 period, for which the trends are highly significant, nitrate loads increased on average by about 7% per year (compared to their initial values) in the Ebro River, and by about 5% per year in the Po and Rhone rivers.

For the Danube, the nitrate record is less complete and only starts in the late 1980s, with a general tendency towards decreasing loads. This is different compared to the Mediterranean rivers, still showing increasing fluxes at this time (Fig. 5a). The start of the NO_3 decrease in the Danube coincides with the breakdown of the communist regimes in the eastern countries, and hence also the abrupt abandon of the collectivistic farming system. One can notice in Figure 4 that the overall fertilizer spreads in the Black Sea drainage basins were lower in 1995 than in 1970, contrary to all drainage basins of the Mediterranean Sea. Before 1990, data on nitrate in the Danube are not available. The only source is the reconstruction of the DIN fluxes that was made in the Danubs project (e.g., Behrendt et al., 2005), but this only allows quantification of the average loads within 5 year time slices and most of the data are model outputs. Also here, observations between 1970 and 1990 were missing. The Danubs modelling revealed

ACCEPTED MANUSCRIPT

an about twofold increase of the DIN loads between 1960 and 1985 before they decreased. The average values, however, were about 50-100% lower than those reported by Garnier et al. (2002a) for similar time periods in the 1990s (Behrendt et al., 2005), making it difficult to link the Danubs loads to more recent data.

Phosphate trends are more diversified (Fig. 5b). There is a strong increase of phosphate loads in the Mediterranean rivers at the beginning of the 1970s, even more pronounced than for nitrate (approximately two times the nitrate increase). But already 10 to 20 years later, this evolution stops and the values decrease. It is remarkable that the phosphate concentrations in the late 1990s declined to about the levels of the early 1970s. For the Rhone, the records do not go back that far in time, but the behaviour similar to the other rivers in later years indicate that this river also followed the general trend. The start of the phosphate decline, however, can be different. It started earliest in the Po (about 1980), followed by the Rhone (around 1985), and finally by the Ebro and Danube (after 1990). This can reflect time lags in combating phosphorus pollution in the different countries, such as the banning of phosphorus detergents, and/ or the upgrading of waste water treatment plants. In the case of the Ebro River, it is also possible that the improvement of the water quality has been delayed by the multitude of reservoirs in this basin, which may have retained older phosphorus loads. Again, the evolution of phosphate in the Danube is different compared to the other large rivers. Here, the curve in Figure 5b does not clearly show a convex shape and the rapid decline after 1990 is synchronous with the decrease of the nitrate loads. This indicates that also the phosphate decline is related to the profound economical and societal changes in the formerly communist countries at the end of 1980.

The disconnected time evolutions of the nitrate and phosphate loads in the Mediterranean rivers had a strong impact on their average nutrient ratios. Molar N-NO_3 to P-PO_4 ratios for individual rivers could have varied within one order of magnitude over the considered 40 years (Fig. 5c). In a very general way, the evolution can be characterized by a polynomial fit between the annual averages of the three Mediterranean rivers and time (x = number of years after 1960):

$$N\text{-}NO_3 / P\text{-}PO_4 = 0.1640\, x^2 - 6.73\, x + 96.4 \qquad (r^2 = 0.90,\ n = 35) \quad \text{(ii)}$$

According to this fit, the early 1980s were the years with the lowest N-NO_3/ P-PO_4 ratio. But even if the general trends are similar in all rivers, the average values for individual rivers could be different. The N-NO_3/ P-PO_4 ratios in the Po were on average often twice as great as in the Rhone and Ebro rivers, in particular during 1985 – 1995. This could reflect an earlier phosphate decline based on the country specific measures to combat phosphorus pollution, but it is also possible that the greater ratios in the Po River relate to the intense agricultural land use in this river basin, releasing greater amounts of DIN to the surface water than in most other Mediterranean rivers.

Phosphate concentrations were more variable over time than the concentrations of nitrate and the general evolution of the N-NO_3/ P-PO_4 ratio was mainly controlled by changes of phosphate. Severe reductions of the riverine phosphorus loads are a widespread phenomenon in Europe, and concentrations in the rivers of the EU and accession countries strongly declined during the 1990s, with greatest reductions in areas with formerly high phosphorus concentration (Crouzet et al., 1999). At the same time, nitrate remained high, and the beginning of a decreasing trend is only limited to very recent years. When reconstructing the N and P loads in the Seine and Scheld rivers by combining model results and observed data, Billen and

ACCEPTED MANUSCRIPT

Garnier (2007) found very similar evolutions as we present for the Po, Rhone and Ebro rivers.

For the Danube, and probably also other east European rivers, equation (ii) may not be valid. The short record in Figure 5c is not very conclusive in this respect, but since phosphate does not show elevated values in the early 1980s, nitrate should have been very low in order to meet the low N-NO_3/ P-PO_4 ratios that are characteristic during that time in the other rivers. The Danubs reconstruction (Behrendt et al., 2005) revealed that N-NO_3/ P-PO_4 ratios were rather constant from 1960 – 1990, but at clearly more elevated levels than in the Mediterranean rivers. Again, these data are modelled data and have a coarse temporal resolution, but they represent the only estimates of nutrient loads in the Danube during the communist regimes.

Additional support that the above reported trends may be representative for the entire Mediterranean and Black Sea region is obtained from statistical analyses of the *Waterbase* data. This database also includes older measurements of annual nitrate and phosphate concentrations in South and East European rivers, but most of the stations are far upstream the river mouths and not associated with corresponding discharge measurements, which does not allow flux calculations. Nevertheless, when considering box plot distributions of the average concentrations within five year time slices (Fig. 6), it can be noticed that the general evolutions towards increasing nitrate values are well reproduced, probably matching the flux increases in the large rivers somewhere between the 50 and 75 percentiles. The outstanding behaviour of the Danube River is confirmed by additional data on Black Sea rivers, showing that both the 50 and 75 percentiles are continuously decreasing after 1990. This is a strong argument that the early decline of nitrate in the Danube was not an isolated case and likely related to the economical changes.

Also the general evolution of the N-NO_3/ P-PO_4 ratios fits well with the observations in the large rivers, even if the median values are lower on average than the ratios in Figure 5c. The evolutions of the 75 and 95 percentiles seem to better fit with the observations in the Po, Rhone and Ebro rivers than the median values. The particular behaviour of the Black Sea rivers is supported by the strong increase of N-NO_3/ P-PO_4 after 1990, followed by a slight decrease in the 1995 – 2000 period. This fits nicely with the observations in the Danube, where the decline of phosphate was at the beginning more abrupt than the decline of nitrate. As in the Danube, the average N-NO_3/ P-PO_4 ratios were also more elevated compared to the Mediterranean rivers before 1990, at least for the extremes (75 and 90 percentiles). But finally in 2000 – 2005, the statistics show quite similar distributions between the Mediterranean and Black Sea rivers, indicating that the economical switch from "eastern to western" conditions was rapidly followed by river geochemistry.

4.4 Silica fluxes

Silica fluxes are difficult to reconstruct over time as this parameter is not often measured by monitoring programs on the water quality of rivers. In contrast to nitrate and phosphate, dissolved silica is almost exclusively derived from chemical weathering of rocks and soils, even if minor contributions from anthropogenic point sources have been reported as well (e.g. Sferratore et al., 2006). It is hence considered as a natural element in surface waters and not regarded as an indicator of pollution. However, there is increasing awareness that the phenomenon of eutrophication in freshwaters and coastal waters is not only depending on the

ACCEPTED MANUSCRIPT

degree of anthropogenic nutrient enrichment, but also on the relative nutrient composition (Cloern, 2001). In particular the unbalance of nitrogen and phosphorus with respect to silica seems to play a crucial role, as it can provoke a shift in primary production from diatoms to non-siliceous algae, often harmful for the ecological equilibrium (Billen and Garnier, 2007, and references therein).

For our review, we could not find representative time series on silica levels in Mediterranean rivers. Only for the Danube, Garnier et al. (2002a) report continuous measurements from 1980 – 1995 at the river mouth that were done by Cosiasu et al. (1996). These data show a slight decrease of the silica loads. For general budget calculations, silica fluxes to the Mediterranean and Black Sea have therefore to be derived indirectly by coupling them to the environmental factors that control the transfer of this element to the sea. Concentrations of Si in rivers are normally less variable than other dissolved nutrients, making that the fluxes of this parameter are largely dominated by water discharge. As a consequence, large scale estimates are commonly obtained by multiplication of the latter with a representative average silica concentration in river water (e.g., Cotrim da Cunha et al., 2007)

An overview of silica levels in different world rivers was obtained by the UNEP/ GEMS monitoring program, confirming the dominant control of runoff on the specific silica fluxes (Table 7). According to this data compilation, the average riverine Si concentration is close to 4 mg Si l^{-1}, as this has also been proposed in other studies (e.g. Treguer et al., 1995, with 4.2 mg Si l^{-1}). Turner et al., 2003 reported that variability of silica concentrations can be controlled by runoff too, since higher values may provoke a dilution effect. On the other hand, the authors also noted generally higher concentrations in low latitude rivers, probably translating the temperature dependency of the weathering reactions (Lasaga, 1998). It can be seen in Table 7 that a simple grouping of the rivers according to their average basin temperatures results in systematically higher Si averages in the warmer basin groups. In particular the comparison of the cold and intermediate temperature groups is interesting. Both have about the same runoff, while the average Si concentration is clearly lower in the colder basins. This is in agreement with the findings of Humborg et al. (2002) who noted generally low weathering fluxes in boreal river systems.

In the warmer subtropical and tropical zones, climate may be more favourable for silicate weathering and runoff becomes the dominant controlling factor. The increasing correlation between the specific silica fluxes and runoff in the warmer climate groups in Table 7 supports this. The Mediterranean has a pivot position between the temperate and subtropical climates, and temperatures are generally higher than in the pure temperate climate further to the north. Consequently, Billen and Garnier (2007) also found higher values in Mediterranean rivers compared to temperate climate rivers after analysis of additional river data. We therefore believe that the temperature dependent selection of representative average silica concentrations in Table 7 to be used with runoff is the best method for estimation of average silica yields

This remains nevertheless a very general approach that cannot account for the influence of other controlling factors, such as the nature of the weathered rock types in the drainage basins. Moreover, anthropogenic factors that can modify the natural riverine silica loads are not accounted for. This mainly concerns the construction of major dams and the subsequent sequestration of dissolved Si in the reservoir sediments through enhanced diatom growth (Schelske and Stoermer,

ACCEPTED MANUSCRIPT

1971). When eutrophication conditions are favourable for diatom growth, silica retention can also occur in large rivers (Sferratore et al., 2006).

There is an ongoing controversy about the effect of "Iron Gate I" on silica in the Danube River, as this reservoir has been postulated to retain about two third of the incoming fluxes (Cociasu et al., 1996; Humborg et al., 1997), whereas more recent studies (McGinnis et al., 2006; Teodoru et al, 2006) on the reservoir sediments seriously questioned this value. But even if the effect of this particular dam may have been overestimated, it likely that reservoir constructions reduced the riverine silica inputs to the Mediterranean and Black Sea during recent decades. Damming of the Nile River alone should have reduced the Si delivery to the Mediterranean by 100×10^3 t yr^{-1} (Nixon, 2003), representing probably about 10% of the overall inputs (see below). Of course, the Aswan High Dam is particular because of its extremely long water residence time, one of the principal conditions for efficient silica trapping in the sediments. But also elsewhere in Mediterranean drainage basin, water retention behind major dams progressed very rapidly since the 1960s (Fig. 7), now intercepting more than 20% of the annual freshwater fluxes by rivers (when counting the Aswan Dam too, this value is 75%).

4.5 Large-scale evolution of nutrient budgets

The elements assembled above finally allow reconstructing the nutrient delivery to the Mediterranean and Black Sea by rivers. The basin delineation shown in Figure 1 was the geographical basis for this reconstruction. We started with nitrate, the nutrient form for which the budgets are the easiest to construct. Several modelling approaches have been published in order to predict the spatial variability of DIN fluxes on the basis of economic and demographic input data (e.g. fertilizer spreads). We used the NEWS-DIN model of Dumont et al. (2005), after adjusting and recalibrating it for the rivers in Table 6 (except the Aude and Herault river basins, which are too small to be properly identified in Fig. 1) The adjustment was the removal of a variable accounting for dammed reservoir retention and the modelling of $N\text{-}NO_3$ instead of DIN. The reservoir variable was removed because the availability of information on dams is not sufficient at the scale of the Mediterranean and Black Sea rivers. The recalibrated model predicts $N\text{-}NO_3$ export (kg N yr^{-1}) in 1998 for every coastal grid cell in a 0.5 by 0.5 degree resolution. The year 1998 was selected because some of the input parameters were only available for this year. As the data in Table 6 refer to later years (around 2003), we adjusted the data according to the average change rates described below.

Hindcasting of the nitrate fluxes was done through polynominal fits of the change rates of five year average fluxes in the large rivers, normalized to the year 2003 (Fig. 8a). Two curves were fitted; one for the Mediterranean rivers (based on the averages of the Rhone, Po, and Ebro in Fig. 5a) and one for the Black Sea rivers (based on the Danubs reconstruction before 1990 and on the Danube values in Figure 5a after 1990). These curves were applied for each coastal grid cell receiving river inputs from the hinterlands. Phosphate fluxes were derived through corresponding fits of the average $N\text{-}NO_3$/ $P\text{-}PO_4$ ratios (Fig. 8b). The fit for the Mediterranean rivers corresponds to equation (ii), but we assumed the $N\text{-}NO_3$/ $P\text{-}PO_4$ ratio to remain constant for the years before 1970, when data coverage is very poor. Both $N\text{-}NO_3$ and $P\text{-}PO_4$ were then transformed to TN and TP according to the average proportions given in section 4.1. In order to account for the inter-annual flux variations related to the variability of water discharge, we also multiplied the fluxes with a factor that reflects the ratio between the yearly Q values and the five year

ACCEPTED MANUSCRIPT

averages of Q. Finally, silica fluxes were calculated with the representative concentrations in Table 7 and water discharges determined in section 3.5.

Assuming constant N-NO_3/ TN and P-PO_4/ TP ratios throughout the Mediterranean and Black Sea drainage basins is naturally a strong simplification with respect to their spatial variability that can be expected at local and regional scales, in particular in the case of phosphorus. Particulate river loads are spatially much more variable than dissolved loads. However, given the methodological problems mentioned above (section 4.1) for estimation of representative TP loads, we did not include individual data on TP in Mediterranean and Black Sea rivers in our data compilation.

In all of our reconstructions, we replaced the predicted values by the observations in the large rivers whenever this was possible. Consequently, for many parameters and years, about one third to half of the budgets corresponds to observed values. The nutrient supply of the Nile was reconstructed with the average N and P concentrations of Nixon (2003) before and after the dam construction. We also followed his hypothesis that the pre-damming nutrient fluxes may have been successively regained at the end of the last century in parallel with the population growth, with the exception of silica, for which the pre- and post-damming values remained very different (110 and 7.5 × 10^3 t yr^{-1}, respectively). Also for the Danube, we slightly modified the predicted silica fluxes on the basis of the reported values of Garnier et al. (2002a) for 1980 – 1995. These fluxes followed a decreasing trend which was more pronounced than the concomitant decrease of water discharge. Analysis of the relationship between both parameters finally permitted the reconstruction of the silica loads during the entire 1960 – 2000 period. Notice that the decrease rate we found is less than 40% in 40 years.

The resulting nutrient budgets are listed in Table 8, distinguished for the different sub-basins and averaged over 5 years time slices. Maximum inputs to the Mediterranean Sea are about 1100 × 10^3 t N yr^{-1} for nitrogen in the 1990s and 100 × 10^3 t P yr^{-1} for phosphorus in the 1980s. This agrees reasonably well with other estimates. Vollenweider et al. (1996), for example, estimated the river inputs to about 1011 × 10^3 t N yr^{-1} and 137 × 10^3 t P yr^{-1}, respectively. The latter value, however, is greater than our estimate, mainly because of a greater input to the Western Basin. Our budgets for the maximum river inputs are in the same order as the estimated atmospheric inputs listed in Guerzoni et al., 1999 (1068 × 10^3 t N yr^{-1} for DIN and 66 × 10^3 t P yr^{-1} for TIP) and in Markaki et al., 2008 (1246 × 10^3 t N yr^{-1} for DIN and 34 × 10^3 t P yr^{-1} for DIP). But they are clearly lower than the budgets of Bethoux et al. (1998), who quantified the combined inputs from rivers and from the atmosphere to about 5350 × 10^3 t N yr^{-1}, 540 × 10^3 t P yr^{-1}, and 7110 × 10^3 t Si yr^{-1} with 1980 as reference year. The discrepancy is particularly striking for silica fluxes, about seven times greater than our budgets for the river inputs alone. Also atmospheric dust can bring biologically available silica to the sea (for global estimates, see for example Cotrim da Cunha et al. (2007) and references therein), but rivers are normally by far the dominant source.

However, the budgets of Bethoux et al. (1998) are derived indirectly by subtraction of the Atlantic surface water inputs from the deepwater outflows at Gibraltar and strongly depend on the estimates of the nutrient levels in the incoming Atlantic waters. The latter are subjected to important uncertainties which may explain these discrepancies. Another reason is that these budgets should also include the nutrient inputs from other sources such as wastewaters of coastal cities that are

ACCEPTED MANUSCRIPT

directly discharged into the sea. Aertebjerg et al. (2001) compiled data on nutrient loads from a number of coastal hotspot pollution sources (based on UNEP/ WHO, 1999) in the Mediterranean region. These sources alone, corresponding to about 10% of the total Mediterranean population, accounted for nutrient loads of about 260×10^3 t N yr^{-1} and of 75×10^3 t P yr^{-1}. For phosphorus, this is in the same range as the riverine and atmospheric inputs.

Previous studies on riverine supply of nutrients mainly focused on the average budgets and ignored their great temporal variability, as well as the important changes in the nutrient compositions. This can lead to conclusions that are only valid for short periods and which do not allow characterisation of the geochemical functioning of the Mediterranean in general. The uniquely high N/P ratios of the Mediterranean waters (>20) compared to other open ocean averages (15) were frequently attributed to important atmospheric contributions. In the atmospheric deposits, the N/P ratio can be very elevated (60 - 105; Guerzoni et al., 1999, Markaki et al., 2008). Also nitrogen fixation in the surface waters was postulated (Bethoux et al., 2002), which can enhance the N levels too. The fact that the N/P ratios are generally more elevated in the Eastern Basin has been taken as an additional support for this hypothesis, since oligotrophy of the surface waters is more important in the east. However, our data show that high N/P ratios are not incompatible with a riverine source *per se*. The time window when the riverine N/P ratios felt below 20 is relatively short and mainly restricted to the period 1975 – 1985. In the Western Basin, this window was larger, whereas in the Eastern Basin it lasted probably only a few years around 1980. The particularly high ratios in the Po River have a considerable impact on the budgets of the entire Eastern Mediterranean. Most of the deepwater is formed in the southern Adriatic Sea (see above) and the impact of the Po nutrients on the deepwater N/P signatures should be high. Moreover, our data also show elevated N/P ratios in the rivers of the Black Sea. Their water and nutrient discharge to the Mediterranean may have increased the N/P ratios too. The riverine signatures are therefore not in contradiction with generally higher N/P levels in the east than in the west.

4.6 Biological implications

Considering the marine primary production that can be supported by the riverine nutrient inputs (PPR) with a Redfield Ratio of C:N:P = 106:16:1 (Redfield et al., 1963), our data suggest that both the Mediterranean and the Black Sea river loads were mostly phosphorus limited during the study period. The period before the general decline of the P loads in the late 1980s is therefore the only period when the anthropogenic nutrient enrichment in rivers allowed additional fertilization of the marine productivity. During this time, PPR increased by a factor of 4 to 6 in most of the Mediterranean basins (Table 8), but remained relatively constant in the Black Sea. Also N limitation could occur in the Western Mediterranean in the early 1980s, when the N and P enrichments were still moderate and N/P ratios could fall below the Redfield Ratio. The postulated N limitation at the beginning of the 1960s in the South-Levantine Basin is rather an exception. It is related to the Nile inputs, which were particularly rich in P before the dam construction (Nixon, 2003)

Mean annual gross primary production (PP) in the Mediterranean Sea is estimated to about 110 – 120 g C m^{-2} for the Eastern Basin and to about 120 – 160 g C m^{-2} for the Western Basin (Bethoux et al., 1998; Crispi et al., 2002; Bosc et al., 2004). In the Black Sea, it is in the range of 130 – 200 g C m^{-2} (Grégoire and Beckers, 2004; Demidov, 2008; Sorokin, 1983). The maximum PPR in Table 8 therefore account only for about 1-2 % (Mediterranean) and 3-5% (Black Sea) of these values,

ACCEPTED MANUSCRIPT

respectively. In the coastal areas with large rivers, however, PPR can be much more important. Taken the Gulf of Lions in the Western Mediterranean as an example, the nutrient inputs from Rhone alone could support between 23% (1960 – 2000 average) and 69% (1960 – 2000 maximum) of the average PP in this region (based on the area and net PP estimates (150 g C m^{-2}) of Sempéré et al., 2000). Indicators that the changing river nutrient loads may have had an impact on biological productivity can therefore be expected in the more productive coastal systems, such as the Adriatic Sea, where PPR is greatest on the basin scale (Table 8).

In this sense, it is interesting to compare our results with the study of Sagiori and Donders (2004) who reconstructed the eutrophication history in the north-western Adriatic Sea during the last 150 years based on high resolution sediment core analyses. They concluded that eutrophication was at its maximum in 1978. This coincides well with our data, showing that 1981 was the year when the P loads of the Po River were greatest (Fig. 5). Moreover, also Solic et al. (1997) reported steadily increasing primary production rates in the northern Adriatic Sea from 1960 to 1980, the period when anthropogenic enhancement of riverine phosphorus loads was greatest.

The temporal evolution of the river Si loads could have influenced the marine productivity too. As mentioned above, Si has only to be considered as a limiting nutrient for diatoms, for which the Redfield Ratio can be enlarged to C:N:Si:P = 106:16:16:1 (Brzezinski, 1985). Shortening of this element does therefore not necessarily reduce the productivity of the marine ecosystems, but it can provoke a switch from diatom dominated communities to non siliceous algae forms, often accompanied by the occurrence of toxic species and reduced fish catches. When determining the limiting element in the river nutrient loads for marine diatoms (Fig. 9), the Mediterranean, PPR was phosphorus limited only during the 1960s and 1970s, before it generally switched to Si limitation in the late 1970s (Fig. 9). In the Black Sea, Si limitation for PPR already started in the mid-1960s. This is particularly interesting because of the shift from diatoms to non-siliceous phytoplankton species that has been observed in the Black Sea in the early 1970s. The shift was widely attributed to the trapping of silica in the "Iron Gate I" reservoir on the Danube after its construction in 1972 (Humborg et al., 1997), although our data indicate that Si limitation began before the dam construction. This is contradicting the trapping hypothesis, even if it does not exclude that additional Si sequestration in reservoirs may have increased its limitation. As reported above, Si fluxes in the Danube decreased indeed over time, despite the more or less constant water discharge. However, even without this decreasing trend, Si limitation would have occurred in about the same years. Its early start in the Danube is in fact related to the low Si/P ratios at the beginning, and even slight increases of the P levels were sufficient to push this ratio below the Redfield Ratio.

In the 1990s, both in the Mediterranean and in the Black Sea rivers, phosphorus became then again the limiting element for PPR. The period when this exactly happened depends on the decrease rate of silica. In our reconstruction, we did not include a general damming effect, and the reductions in the fluxes of silica are mainly driven by the decrease of discharge. Supposing an additional Si decrease of 30% because of reservoir retention would delay P limitation by about 5 years. But it is not likely that silica limitation continued beyond the year 2000. Its decline is rather smooth and cannot compete with the abrupt decrease of the phosphorus levels. Of course, more observations are needed to confirm this, but recent data on European rivers show that the strong reduction of anthropogenic P continues (see also Table 6), and probably into the near future. According to Billen and Garnier

ACCEPTED MANUSCRIPT

(2007), a prospective scenario corresponding to the application of the European Water Framework Directive (WFD, 2000) may involve a 90% abatement of phosphorus from all urban wastewater inputs by 2015. This means that the phosphorus levels in the Mediterranean and Black Sea rivers could fall far below the 1960 levels.

5. Conclusions

This review of the major hydrological and geochemical characteristics of Mediterranean and Black Sea rivers was intended to quantify the delivery of water and nutrients to the sea. The regional budgets we established not only include the spatial variability of fluxes, but also for the first time their temporal variability over the last 4 decades (1960-2000+). We recognize that such general estimates cannot take into account the numerous peculiarities and strong small-scale heterogeneity characterizing Mediterranean and Black Sea rivers. But these budgets clearly demonstrate that river discharges underwent marked changes during the last decades, both in quantity and composition, potentially identifying them as major drivers of the geochemical, physical and biological functioning of the marine system in this part of the world ocean.

Over the 1960-2000 period, river freshwater discharge to the Mediterranean Sea decreased, while that to the Black Sea remained more or less constant. For the former, we estimate the reduction to be at least 20%, with no major differences between the eastern and western basins. This reduction is mainly derived from the large-scale evolution of precipitation and temperature and thus reflects the potential impact of climate change on river freshwater discharge. Trend analyses on a set of Mediterranean rivers confirm the decrease, but the discharge reductions are often more drastic than estimates from climate parameters alone. In particular, in the drier parts of the Mediterranean drainage basin, anthropogenic water use can additionally reduce the long-term water flow in rivers, so our estimate for the total reduction of the freshwater discharge to the Mediterranean Sea is probably a minimum. Nevertheless, given the strong importance of water resources for local economies in this part of the world, already a 20% reduction in only 40 years is highly remarkable. This underlines why the Mediterranean region was identified as one of the most prominent “hot-spots” in future climate change projections (Giorgi, 2006).

The evolution of river fluxes of nutrients exhibits opposite trends between increasing nitrogen and phosphorus fluxes, both enhanced via anthropogenic activities in the drainage basins, and the fluxes of silica, mainly controlled by natural rock weathering and subject to a decreasing trend via the reduction of freshwater fluxes and massive dam constructions. However, the anthropogenic nutrients do not follow exactly the same trends. Efforts undertaken to mitigate point source pollutions in the 1980s and 1990s had an immediate impact on the phosphorus loads, in particular in European rivers. After a dramatic increase in the 1960s and 1970s, phosphorus rapidly declined to early 1960s levels. The pattern is somehow different for nitrogen, mainly released via diffuse sources such as fertilizers. Nitrogen followed more or less a continuous increase over the study period, before starting to decrease only recently. With regard to the situation in 1960, Mediterranean and Black Sea rivers are nowadays characterized by a strong excess of nitrogen over phosphorus and silica.

ACCEPTED MANUSCRIPT

Our vision could appear as being biased by the better data coverage on European rivers in the North compared to data sets from African and Middle-Eastern rivers, which perhaps evolved differently. But it has to be kept in mind that European rivers account for most of the total river fluxes. The Rhone and the Po alone carry about one third of the riverine freshwater to the Mediterranean Sea, and the Danube discharge accounts for more than half of the inputs to the Black Sea. This gives some robustness to our estimates, at least for nitrogen and phosphorus. Regarding silica, our values and particularly the temporal evolution are more difficult to validate, since long-term time series are missing. But compared to the rapid changes of the phosphorus and nitrogen loads, variations in silica have probably been smoother. Our average budget estimates may include some errors, but they probably do not much affect the qualitative trends detected. Nevertheless, it is evident that regular measurements of silica in rivers, so far mostly ignored in monitoring programs of water quality, should be included in future surveys.

A detailed evaluation of the possible impact of the changing loads of Mediterranean and Black Sea rivers on the corresponding marine ecosystems is difficult and beyond the scope of the present work. Nutrients from rivers sustain only <2% of the overall gross primary production in the Mediterranean Sea and <5% in the Black Sea. However, quantitative and qualitative changes in primary production concomitant with changes in nutrient inputs have been reported in the more productive coastal areas that receive major river inputs, such as the Adriatic Sea and the north-western part of the Black Sea. Further work including new data and modelling is clearly needed to define if this may have also occurred at other places. Modelling studies are also needed to evaluate the potential impact of the reductions in freshwater inputs on marine ecosystems through modifications of the water circulation in the Mediterranean Sea.

6. Acknowledgements

Research for this paper was supported by the European Commission within the Sixth Framework Programme on Sustainable Development, Global Change and Ecosystems (project SESAME, Contract No GOCE-036949). CRU kindly supplied the gridded temperature and precipitation data sets and E. Lemeshko (MHI UNAS Sevastopol) is acknowledged for the discharge data of the Dniepr River. We are grateful for the valuable comments of S.V. Smith and two anonymous reviewers on previous versions of the manuscript.

7. References

Abu El Ella, E.M., 1993. Preliminary studies on the geochemistry of the Nile river basin, Egypt. In: S. Kempe, D. Eisma and E.T. Degens (Eds), Transport of Carbon and Minerals in Major World Rivers, part 6, Mitt. Geol.-Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband 74, Hamburg, pp. 115-135.

Algan, O., 2006. Riverine fluxes into the Black and Marmara Seas. In: F. Briand (Ed.) Fluxes of small and medium-size Mediterranean rivers: impact on coastal areas. CIESM Workshop Monographs 30, pp. 47-53.

Amoros, G., Petts, G.E. (Eds.), 1993. Hydrosystèmes Fluviaux. Masson (Collections d'Ecologie), Paris, 300 pp.

Aertebjerg, G., Carstensen, J., Dahl, K., Hansen, J., Nygaard, K., Rygg, B., Sorensen, K., Severinsen, G., Casartelli, S., Schrimpf, W., Schiller, C., Druon, J.N., 2001. Eutrophication in Europe's coastal waters. European Environmental Agency, Topic report 7 (can be downloaded at: http://www.eea.europa.eu/).

ACCEPTED MANUSCRIPT

Attané, I., Courbage, J., 2001. La démographie en Méditerranée. Situation et projections. Les Fascicules du Plan Bleu, 11. Paris, Economica, 249 pp.

Behrend, H., van Gils, J., Schreiber, H., Zessner, M., 2005. Point and diffuse nutrient emissions and loads in the transboundary Danube Riber Basin. – II Long-term changes. Archiv für Hydrobiologie - Supplement 158, 221-247.

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

Bethoux, J.P., Morin, P., Chaumery, C., Connan, O., Gentili, B., Ruiz-Pino, D., 1998. Nutrients in the Mediterranean Sea: mass balance and statistical analysis of concentrations with respect to environmental change. Marine Chemistry 63, 155-69.

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

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

Bosc, E., Bricaud, A., Antoine, D., 2004. Seasonal and interannual variability in algal biomass and primary production in the Mediterranean Sea, as derived from 4 years of SeaWiFS observations. Global Biogeochemical Cycles 18, GB1005, doi:10.1029/2003GB002034.

Boukthir, M., Barnier, B., 2000. Seasonal and inter-annual variations in the surface freshwater flux in the Mediterranean Sean from the ECMWF re-analysis project. Journal of Marine Systems 24, 343-354.

Brzezinski, M.A., 1985. The Si:C:N ratio of marine diatoms: interspecific variability and the effect of some environmental variables. Journal of Phycology 21, 347–357.

Bouwman A.F., Van Drecht, G., Van de Hoek, K.W., 2005. Global and Regional Surface Nitrogen Balances in Intensive Agricultural Production Systems for the Period 1970-2030. Pedosphere 15 (2), 137-155.

Christensen, J.H., Hewitson, B., Busuioc, A., Chen, A., Gao, X., Held, I., Jones, R., Kolli, R.K., Kwon, W.T., Laprise, R., Magaña Rueda, V., Mearns, L., Menéndez, C.G., Räisänen, J., Rinke, A., Sarr, A., Whetton, P., 2007. Regional Climate Projections. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom.

Cloern, J.E., 2001. Our evolving conceptual model of the coastal eutrophication problem. Marine Ecology Progress Series 210, 223–253.

Cociasu, A., Dorogan, L., Humborg, C., Popa, L., 1996. Long-term ecological changes in Romanian coastal waters of the Black Sea. Marine Pollution Bulletin 32, 32–38.

Conley, D.J., 1997. Riverine contribution of biogenic silica to theoceanic silica budget. Limnology and Oceanography 42, 774–777.

Conley, D.J., Schelske, C.L., 2001. Biogenic silica. In: Smol, J.P., Birks, H.J.B., Last, W.M. (Eds.), Tracking Environmental Change Using Lake Sediments: Biological Methods and Indicators. Kluwer Academic Press, pp. 281–293.

Cotrim da Cunha, L., Buitenhuis, E.T, Le Quéré, C., Giraud, X., Ludwig, W., 2007. Potential impact of changes in river nutrient supply on global ocean biogeochemistry. Global Biogeochemical Cycles, 21, GB4007, doi:10.1029/2006GB002718.

Crispi, G., Crise, A., Solidoro, C., 2002. Coupled Mediterranean ecomodel of the phosphorus and nitrogen cycles. Journal of Marine Systems 33-34, 497-521.

Crouzet, P. Nixon, S., Rees, Y., Parr, W., Laffon, L., Bogestrand, J., Kristensen, P., Lallana, C., Izzo, G., Bokn, T., Bak, J., Lack, T.J., Thyssen, N., 1999. Nutrients in Eyropean Ecosystems. Environmental assessment report, 4, EEA, Copenhagen, 155 pp. (can be downloaded at: http://www.eea.eu.int).

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

Demidov, A.B., 2008. Seasonal Dynamics and Estimation of the Annual Primary Production of Phytoplancton in the Black Sea. Oceanology 48, 664-678.

Doell, P., Lehner, B., 2002. Validation of a new global 30-min drainage direction map, Journal of Hydrology 258 (1-4), 214-231.

ACCEPTED MANUSCRIPT

Dumont, E., Harrison, J.A., Kroeze, C. Bakker, E.J., Seitzinger, S.P., 2005. Global distribution and sources of dissolved inorganic nitrogen export to the coastal zone: Results from a spatially explicit, global model. Global Biogeochemical Cycles 19, GB4S02, doi:10.1029/2005GB002488.

EEA, 2007. Waterbase, v7. (data can be dowloaded at: http://dataservice.eea.europa.eu/dataservice/metadetails.asp?id=984).

Foellmi, K.B., 1996. The phosphorus cycle, phosphonenesis and marine phosphate-rich deposits. Earth Science Reviews 40, 55-124.

Garnier, J., Billen, G., Hannon, E., Fonbonne, S., Videnina, Y., Soulie, M., 2002a. Modelling the transfer and retention of nutrients in the drainage network of the Danube River. Estuarine, Coastal and Shelf Science 54, 285–308.

Garnier, J., d'Ayguesvives, A., Billen, G., Conley, D., Sferratore, A., 2002b. Silica dynamics in the hydrographic network of the Seine River. Oceanis 28, 487–508.

Gibelin, A.L., Déqué, M., 2003. Anthropogenic climate change over the Mediterranean region simulated by a global variable resolution model. Climate Dynamics 20, 327-339.

Giorgi, F., 2006. Climate change hot-spots. Geophysical Research Letters 33, L08707, doi: 10.1029/2006GL025734.

Giorgi, F., Lionello, P., 2008. Climate change projections for the Mediterranean region. Global and Planetary Change 63, (2-3), 90-104.

Grégoire, M., Beckers, J.M., 2004. Modeling the nitrogen fluxes in the Black Sea using a 3D coupled hydrodynamical-biogeochemical model: transport versus biogeochemical processes, exchanges across the shelf break and comparison of the shelf and deep sea ecodynamics. Biogeosciences 1, 33-61.

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., Ziveri, P., 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. Progress in Oceanography 44, 147-190.

Holdridge, L.R., 1959. Simple method for determining potential evapotranspiration from temperate data. Science 130, 572.

Hopkins, T.S., 1985. Physics of the Sea. In: Margalef, R. (Ed.) Western Mediterranean. Pergamon Press, Oxford, pp. 100-125.

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

Humborg C., Blomqvist S., Avsan E., Bergensund Y., Smedberg E., Brink J., Mörth, C.M., 2002. Hydrological alterations with river damming in northern Sweden: Implications for weathering and river biogeochemistry. Global Biogeochemical Cycles 16, 1039, doi: 10.1029/2000GB001369.

Hydro, 2006. (data can be downloaded at: http://www.hydro.eaufrance.fr/)

Ibanez, C., Prat, N., Canicio, A., 1996. Changes in the hydrology and sediment transport produced by large dams on the lower Ebro River and its estuary. Regulated Rivers: Research & Management 12, 51-62.

IPCC, 2001. Climate Change 2001. The scientific basis. In: Houghton J.T., Ding, Y., Griggs, D.J., Noguer, M., Van der Linder, P.J., Dai, X., Maskell, K., Johnson, C.A. (Eds) Contribution of working group I to the third assessment report of the IPCC. Cambridge University Press, Cambridge, 881 pp.

Jaoshvili, S., 2002. The rivers of the Black Sea. EEA Technical report 71, European Environmental Agency, 58 pp. (can be downloaded at: http://reports.eea.europa.eu/technical_report_2002_71/en).

Kendall, M.G., 1975. Rank Correlation Measures. Charles Griffin, London.

Kniewald, G., Margus, D., and Mihelcic, G., 2006. Formation of the Krka river estuary in Croatia and the travertine barrier phenomenon. In: Briand, F. (Ed.), Fluxes of small and medium-size Mediterranean rivers: impact on coastal areas. CIESM Workshop Monographs 30, pp. 93-95.

Korzoun, V.I., Sokolov, A.A., Budyko, M.I., Voskresensky, G.P., Kalinin, A.A., Konoplyantsev, E.S., Korotkevich, E.S., Lvovich, M.I., 1977. Atlas of World Water Balance. UNESCO Press, Paris, 36 pp.

Lasaga, A., 1998. Kinetic Theory in the Earth Science. Princeton University Press.

ACCEPTED MANUSCRIPT

Lascaratos A., Roether, W., Nittis, K., Klein, B., 1999. Recent changes in deep water formation and spreading in the eastern Mediterranean Sea: a review. Progress in Oceanography 44, 5–36.

Lespinas, F. 2008. *Impacts du changement climatique sur l'hydrologie des fleuves côtiers en région Languedoc-Roussillon*. Thèse de Doctorat, Université de Perpignan Via Domitia, 334 pp.

Ludwig, W., Meybeck, M., Abousamra, F., 2003. Riverine transport of water, sediments, and pollutants to the Mediterranean Sea. UNEP MAP Technical report Series 141, UNEP/ MAP Athens, 111 pp. (can be downloaded at: http://www.unepmap.org/).

Mann, H.B., 1945. Non-parametric tests against trend. Econometrica 13, 245-259.

Margat, J., Treyer, S, 2004. L'eau des Méditerranéens: situation et perspectives. MAP Technical Report Series No. 158, 366 pp. (can be downloaded at: http://www.unepmap.org/).

Markaki, Z., Loÿe-Pilot, M.D., Violaki, K., Benyahya, L., 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, Marine Chemistry, doi:10.1016/j.marchem.2008.10.005.

McGinnis, D. F., Bocaniov, S. Teodoru, C., Friedl, G., Lorke, A., Wüest, A., 2006. Silica retention in the Iron Gate I reservoir on the Danube River: The role of side bays as nutrient sinks. River Research and Applications 22, 441–456.

Medhycos, 2001. The Mediterranean hydrological cycle observing system. Medhycos phase II, period 2002-2005, report no. 17, 36 pp.

Meybeck, M., 1982. Carbon, nitrogen and phosphorus transport by world rivers. American Journal of Science 282, 401-450.

Milliman, J.D., 2001. Delivery and fate of fluvial water and sediment to the sea: a marine geologist's view of European rivers. Scientia Marina 65 (Suppl. 2), 121-132.

Milly ,P.C.D, Dunne K.A, Vecchia, A.V., 2005. Global Pattern of trends in streamflow water availability in a changing climate. Nature 438, 347-350.

Mitchell, T.D., Jones, P.D., 2005. An improved method of constructing a database of monthly climate observations and associated high-resolution grids. International Journal of Climatology 25, 693–712.

Munoz, I., Prat, N., 1989. Effects of river regulation on the lower Ebro River, Northeast Spain. Regulated rivers: research & management 3(1-4), 345-354.

Newbold, J.D., Elwood, J.W., O'Neill, R.V., l98l. Measuring nutrient spiralling in streams. Canadian Journal of Fisheries and Aquatic Sciences 38, 860-863.

Norrant, C., Douguédroit, A., 2005. Monthly and daily precipitation trends in the Mediterranean (1950-2000). Theoretical and Applied Climatology, DOI10.1007/s00704-005-0163-y.

Nixon, S.W., 2003. Replacing the Nile: Are Anthropogenic Nutrients Providing the Fertility Once Brought to the Mediterranean by a Great River? Ambio 32, 30-39.

Pike, J.G., 1964. The estimation of annual runoff from meteorological data in a tropical climate. Journal of Hydrology 2, 116-123.

PNUE, 2001. L'urbanisation en Méditerranée de 1950 à 1995. Sophia Antipolis : Les Cahiers du Plan Bleu 1, PNUE. PAM. Plan Bleu, 45 pp.

Pont, D., 1996. Evaluation des charges polluantes du Rhône à la Méditerranée. Synthèse et recommandations. Agence de l'Eau Rhône-Méditerranée-Corse, Lyon, 350 pp.

Redfield, A.C., Ketchum, B.H., Richards, F.A., 1963. The influence of organisms on the composition of sea-water. In: Hill, M.N. (Ed.), The Sea. John Wiley & Sons, New York, pp. 12–37.

Sagiori, F., Donders, T.H., 2004. Reconstructing 150 years of eutrophication in the north-western Adriatic Sea (Italy) using dinoflagellate cysts, pollen and spores. Estuarine, Coastal and Shelf Science 60, 69-79.

Schelske, C.L., Stoermer, E. F., 1971. Eutrophication, silica depletion, and predicted changes in algal quality in Lake Michigan. Science 173, 423-424.

Sen, P. K., 1968. On a class of aligned rank order tests in two-way layouts. Annals of Mathematics and Statistics 39, 1115-1124.

Seitzinger, S.P., Harrison, J. A., Dumont, E., Beussen, A., Bowman, A.F., 2005. Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of

ACCEPTED MANUSCRIPT

Global Nutrient Export from Watersheds (NEWS) models and their application. Global Biogeochemical Cycles 19 , GB4S01, doi:10.1029/2005GB002606.

Skliris, N., Sofianos, S., Lascaratos, A., 2007. Hydrological changes in the Mediterranean Sea in relation to changes in the freshwater budget: A numerical modelling study. Journal of Marine Systems 65, 400-416.

Skoulidikis, N. T., Gritzalis, K., 1998. Greek river inputs in the Mediterranean. Their intra-annual an inter-annual variations. Fresenius Environmental Bulletin 7, 90-95.

Smith, S. V., Swaney, D. P., Talaue-McManus, L., Bartley, J. D., Sandhei, P. T., McLaughlin, C., Dupra, V. C., Crossland, C. J., Buddemeier, R. W., Maxwell, B. A, Wulff, F., 2003. Humans, hydrology, and the distribution of inorganic nutrient loading to the ocean. Bioscience 53, 235-245.

Smith, S. V., Swaney, D. P, Buddemeier, R. W., Scarsbrook, M.R., Weatherhead, M.A., Humborg, C., Eriksson, H., and Hannerz, F., 2005. River nutrient loads and catchment size. Biogeochemistry 75, 83–107.

Snoussi, M, Haïda, S., Imassi, S., 2002. Effects of the construction of dams on the water and sediment fluxes of the Moulouya and the Sebou Rivers, Morocco. Regional Environmental Change 3, 5–12.

Solic M., Krstulovic N., Marasovic I., Baranovic A., Pucher-Petkovic T., Vucetic T., 1997. Analysis of time series of planktonic communities in the Adriatic Sea: distinguishing between natural and man-induced changes. Oceanologica Acta 20, 131–143.

Somot, S., Sevault, F., Déqué, M., 2006. Transient climate change scenario simulation of the Mediterranean Sea for the twenty-first century using a high-resolution ocean circulation model. Climate Dynamics 27, 851–879.

Sorokin, Yu. I., 1983. The Black Sea. In: Ketchum, B. H. (Ed.), Estuaries and Enclosed Seas. Ecosystems of the World. Elsevier, New York, pp. 253–292.

Tartari, G., Milan, C., Elli, M. (1991). Hydrochemistry of the nutrients. In: Atti del Convegno (Ed.), Quality of the Po River waters during the 1990s (Ferrara 18-20 April). Quad Ist Ric Acque 92, Rome, pp. 6.1-6.29.

Teodoru, C., Dimopoulos, A., Wehrli, B., 2006. Biogenic silica accumulation in the sediments of the Iron Gate I reservoir on the Danube River. Aquatic Sciences 68, 469–481.

TNMN, 2002. TransNational Monitoring Network. Water quality in the Danube River basin. TNMN yearbook 2002 (can be downloaded at: http://www.icpdr.org/icpdr-pages/tnmn_yearbooks.htm).

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 (5209), 375 – 379.

Tolmazin, D., 1985. Changing coastal oceanography of the Black Sea, I: Northwestern shelf. Progress in Oceanography 15, 217-276.

Trenberth, K.E., Jones, P.D., Ambenje, P., Bojariu, R., Easterling, D., Klein Tank A., Parker, D., Rahimzadeh, F., Renwick, J.A., Rusticucci, M., Soden, B., Zhai, P., 2007. Observations: Surface and Atmospheric Climate Change. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L., (Eds.), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom.

Turley, C.M., 1999. The changing Mediterranean Sea — a sensitive ecosystem? Progress in Oceanography 44, 387-400.

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.

UNEP, 1978. Provisional inventory data on surface water in the Mediterranean. Meeting of experts on fresh water resources management in the Mediterranean region, Cannes, 25-29. 04. 1978. UNEP/WG. 16/INF.6.

UNEP/WHO, 1999. Identification of priority pollution hot spots and sensitive areas in the Mediterranean'. MAP Technical Reports Series No 124. UNEP, Athens, 90 pp.

USGS, 2000. GTOPO30 - A global 30 Arc-Second Elevation data set. Developed at the U.S. Geological survey EROS Data Centre (available at: http://edcdaac.usgs.gov/ gtopo30/gtopo30.html).

ACCEPTED MANUSCRIPT

Vollenweider, R. A., Rinaldi, A., Viviani, R., Todini, E., 1996. Assessment of the state of eutrophication in the Mediterranean Sea. Mediterranean Action Plan Technical Reports Series, No. 106.

Vörösmarty, C.J., Fekete, B.M., Tucker, B.A., 1998. Global River Discharge 1807-1991, RivDIS v1.1 (available on-line: <http://daacsti.ornl.gov//RIVDIS/guides/rivdis_guide.html>. Last update: June 2004).

Vörösmarty, C. J., Fekete, B. M., Meybeck, M., Lammers, R., 2000a. Geomorphometric attributes of the global system of rivers at 30-minute spatial resolution. Journal of Hydrology 237, 17-39.

Vörösmarty, C. J., Fekete, B. M., Meybeck, M., Lammers, R., 2000b. A simulated topological network representing the global system of rivers at 30-minute spatial resolution (STN-30), Global Biogeochemical Cycles 14, 599– 621.

WFD, 2000. Water Framework Directive. OJ L 327/1, 22.12, pp. 1–72.

Xoplaki, E., Gonzalez-Rouco, J.F., Luterbacher, J., Wanner, H., 2004. Wet season Mediterranean precipitation variability: influence of large-scale dynamics and trends. Climate Dynamics 23, 63–78.

Zanchettin, D., Traverso, P., Tomasino, M., 2008. Po River discharges: a preliminary analysis of a 200-year time series. Climatic Change 89, 411–433.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

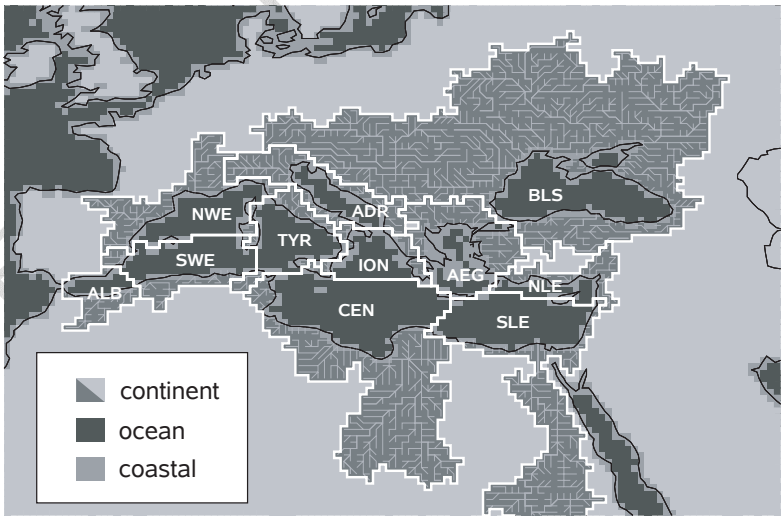
Table 1 *– Characteristics of the Mediterranean and Black Sea drainage basins*

Basin name	Short name	Land area (10^3 km^2)	Sea area (10^3 km^2)	Land/ sea ratio	Mean elevation* (m)	Mean slope* (degree)
Alboran	ALB	111	76	1.46	812	7.3
South-Western	SWE	129	270	0.48	638	3.7
North-Western	NWE	311	252	1.23	696	9.9
Tyrrhenian	TYR	112	242	0.46	443	3.1
Adriatic	ADR	235	131	1.80	782	12.1
Ionian	ION	68	184	0.37	422	6.0
Central	CEN	1135	606	1.87	381	1.0
Aegean	AEG	286	202	1.42	537	6.7
North-Levantine	NLE	131	111	1.18	866	10.5
South-Levantine	SLE	3010	436	6.91	751	2.8
Total Western	WMED	662	840	0.79	661	7.1
Total Eastern	EMED	4864	1669	2.91	653	3.3
Total Eastern**	EMED*	719	1669	0.43	666	9.1
Total Mediterranean	MED	5526	2508	2.20	654	3.8
Total Mediterranean*	MED*	1381	2508	0.55	664	8.1
Black Sea	BLS	2398	460	5.21	398	4.0

* Elevation and slope were taken from USGS (2000).

** without CEN and SLE.

Delineation of the basins was done according to Döll and Lehnert, 2002 (see Figure to the right). The CEN basin in the south corresponds to a potential drainage basin, which is not active because of the very dry climate (desert). This explains the difference with Figure 1.



ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 2 *– Average freshwater fluxes to the Mediterranean and the Black Sea*

Basin (1)	Literature averages (km^3 yr^{-1}) – (2)					This study (km^3 yr^{-1})				
	(A)	(B)	(C)	(D)	(E)	Based on trends (3)			Averages	
						1960	2000	sl	1960-1969	1991-2000
ALB	9	6	1			6	2	++	7	3
SWE	12	9	13			10	7	++	9	7
NWE	124	95	101			96	86	+	97	85
TYR	43	39	31			21	18	ns	18	17
ADR	161	164	133			130	112	++	127	118
ION	38	35	26			17	13	ns	12	11
CEN	5	3	4			4	4	ns	4	4
AEG	69	47	48			54	42	++	55	48
NLE	49	25	43			19	18	ns	24	20
SLE	154	17 (47)	339			19	12	++	34	16
BLS	473		413		348* (381)	392	403	ns	396	403
MED	663	440	737	430		390	305	++	387	328
MED* (4)	509	423	399			371	293		353	312

(1) For abbreviations, see Table 1
(2) Sources: (A) Kourzoun et al., 1977; (B) UNEP, 1978; (C) Vörösmarty et al., 1998; (D) Margat et Treyer, 2004; (E) Jaoshvili, 2002 (* not including the Sea of Azov with about 40 km^3 yr^{-1} - Algan, 2006). In brackets: values before major damming
(3) Values correspond to trend projections for the indicated years (see text) at a given significance level (sl; ++ = $P \leq 0.1$, + = $P \leq 0.2$, ns = not significant)
(4) MED* = MED without SLE (Nile River)

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 3 *- Discharge trends in some Mediterranean and Black Sea rivers.*

River	Country	Basin (1)	Station	Area (km^2)	Period start	Period end	mean Q ($m^3 s^{-1}$)	trend (2)	DS (3)
Rhone	France	NWE	Beaucaire	95590	1960	1999	1721.0		(a)
Aude	France	NWE	Moussan	4956	1965	1997	43.8		(c)
Herault	France	NWE	Agde	2577	1966	2004	40.3	-52.6	(c)
Var	France	NWE	Malaussene	1830	1960	2005	37.7	-24.5	(c)
Tet	France	NWE	Perpignan	1357	1971	2004	10.4		(c)
Orb	France	NWE	Beziers	1323	1966	2004	26.9	*-19.6*	(c)
Ebro	Spain	NWE	Tortosa	84230	1960	1999	416.0	-63.5	(a)
Jucar	Spain	NWE	Alcala del Jucar	10785	1975	1999	12.7	-72.9	(a)
Moulouya	Morocco	ALB	Dar el Caid	24422	1960	1988	21.1	-71.5	(b)
Medjerdah	Tunisia	TYR	Ghardimaou	1490	1960	1995	3.9		(b)
Po	Italy	ADR	Pontelagoscuro	70091	1960	1996	1569.3		(a)
Tevere	Italy	TYR	Ripetta	16500	1960	1997	216.8	-36.3	(a)
Adige	Italy	ADR	Boara Pisani	11954	1960	1980	200.5		(a)
Arno	Italy	NWE	San Giovanni	8190	1960	1995	83.6	*-24.5*	(a)
Pescara	Italy	ADR	Santa Theresa	3130	1960	1999	45.8	-50.8	(a)
Ofanto	Italy	ADR	S.Samuele di Cafiero	2720	1960	1999	11.7	-51.2	(a)
Mirna	Croatia	ADR	Portonski most	483	1961	1998	7.6	-31.5	(a)
Krka	Croatia	ADR	Skradinski buk gornji	2285	1960	1998	53.4	-29.0	(a)
Cetina	Croatia	ADR	Tisne stine	1460	1960	1998	32.0	-80.5	(a)
Zrmanja	Croatia	ADR	Jankovica Buk		1961	1990	37.6	*-22.6*	(a)
Vijose	Albania	ADR	Dorze	5420	1965	1984	145.3		(b)
Semani	Albania	ADR	Ura Vajgurore	2070	1960	1989	32.8	-39.3	(a)
Shkumbini	Albania	ADR	Paper	1960	1960	1990	35.3	-41.2	(a)
Erzeni	Albania	ADR	Ndroq	663	1960	1992	13.4	-47.1	(a)
Mati	Albania	ADR	Shoshaj	646	1960	1988	25.3		(a)
Aliakmon	Greece	AEG	Il Arion	5005	1963	1987	50.0		(a)
Vadar	Greece	AEG	Skopje	4650	1961	1998	58.5	-41.9	(a)
Nestos	Greece	AEG	Temenos	4393	1966	1995	39.6	-67.0	(a)
Acheloos	Greece	ION	Avleko	1349	1965	1995	51.4	-35.2	(a)
Aoos	Greece	ION	Konitsa	665	1964	1986	24.3		(a)
Danube	Romania	BLS	Tulcea Ceatal Izmail	807000	1960	2000	6573.8		(a)
Dniepr	ex URSS	BLS	Power Plant	463000	1960	2006	1488.1		(d)
Don	ex URSS	BLS	Rasdorskay	378000	1960	1984	670.9		(b)
Dniestr	ex URSS	BLS	Bendery	66100	1965	1984	376.6		(b)
Kuban	ex URSS	BLS	Tikhovski	48100	1965	1984	317.2	*-18.8*	(b)
Southern Bug	ex URSS	BLS	Aleksandrova	46200	1960	1984	110.5		(b)
Rioni	ex URSS	BLS	Sakochakidze	13330	1960	1984	408.5		(b)

(1) For abbreviations, see Table 1
(2) The significance level for trends was $P \leq 0.1$ ($P \leq 0.2$ for values in italic). No value means that trends were not significant. The unit is % of the discharge at the beginning of the reference period.
(3) DS - data sources: (a) Medhycos (2001); (b) Vörösmarty et al. (1998), (c) HYDRO (2006), (d) E. Lemeshko, MHI UNAS Sevastopol (pers. com.)

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 4 *– Results of trend analyses on hydroclimatic parameters in the Mediterranean and Black Sea drainage basins*

Basin	Precipitation		Temperature		Q-Pike	
	1960-2000 average (mm)	1960-2000 change (mm)	1960-2000 average (°C)	1960-2000 change (°C)	1960-2000 average (mm)	1960-2000 change (mm)
ALB	401	-165	16.1	1.0	41	-42
SWE	480	*-64*	15.8	1.3	64	-24
NWE	806		11.4	1.3	349	*-64*
TYR	686		14.7	0.9	171	
ADR	1121	*-103*	9.8	0.8	641	-116
ION	784		14.7		226	
CEN	79		21.8	1.2	3	
AEG	645	-87	12.8		170	-47
NLE	616		14.0		140	
SLE	647	-70	25.1	1.3	139	-40
BLS	639		8.4	*0.6*	248	
WMED	654	-71	13.6	1.2	212	-49
EMED	539	-60	22.4	1.3	135	-36
MED	552	-62	21.4	1.2	144	-37

The significance level for trends was $P \leq 0.1$ ($P \leq 0.2$ for values in italic). No value means that trends were not significant. For basin abbreviations, see Table 1

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 5 *– Relative importance of the different nitrogen and phosphorus species in the Po, Rhone and Ebro rivers.*

River	Nitrogen						Phosphorus				source
	TN mg l^{-1}	$N\text{-}NO_3$ %	$N\text{-}NO_2$ %	$N\text{-}NH_4$ %	DON %	PN %	TP mg l^{-1}	$P\text{-}PO_4$ %	DOP %	PP %	
Po	3.1	71.0*			17.0	12.0	0.17	49.0	6.0	45.0	(1)
Rhone	1.7	78.2	1.2	5.4	8.4	6.9	0.12	36.0	18.5	45.5	(2)
Ebro	2.6	75.5	1.1	4.2	11.5	7.7	0.20	58.0		42.0	(3)

* includes also $N\text{-}NO_2$ and $N\text{-}NH_4$; TN = total nitrogen, DON = dissolved organic nitrogen, PN = particulate nitrogen; TP = total phosphorus; DOP = dissolved organic phosphorus, PP = particulate phosphorus.
Sources: (1) Tartari et al., 1991; (2) Pont, 1996; (3) Munoz and Prat, 1989.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 6 *– Average nitrate and phosphate levels in Mediterranean and Black Sea rivers during recent years*

River	basin	Country	av. N-NO_3		av. P-PO_4		Q	F-NO_3	F-PO_4
			(mg l^{-1})	period	(mg l^{-1})	period	(mm)	(kg N km^2 yr^{-1})	(kg P km^2 yr^{-1})
Acheloos	ION	Greece	0.29	01-02	0.010	01	1023	292	10
Aliakmon	AEG	Greece	1.02	01-02	0.125	01-02	123	125	15
Arno	NWE	Italy	2.39	01-05	0.149	01-05	255	609	38
Aude	NWE	France	1.51	00-05	0.107	00-05	290	437	31
Axios	AEG	Greece	1.94	00-02	0.540	00	198	384	107
Danube	BLS	Rumania	2.33	00-02	0.095	00-02	257	599	24
Ebro	NWE	Spain	2.39	00-05	0.065	00-03	110	263	7
Evros	AEG	Greece/ Turkey	1.16	02	1.470	02	124	144	182
Herault	NWE	France	0.58	00, 06	0.023	00, 06	590	340	13
Isonzo	ADR	Italy	1.54	01-05	0.007	01-05	1830	2818	14
Jucar	NWE	Spain	4.01	00-05	0.080	05	58	233	5
Kamjia	BLS	Bulgaria	5.31	00-05	0.146	00-05	113	600	16
Llobregat	NWE	Spain	2.19	01-04			95	208	
Mijares	NWE	Spain	1.07	00-05			79	85	
Neretva	ADR	Croatia	0.66	03-05	0.007	03-05	1169	767	8
Nestos	AEG	Greece	1.58	00-04	0.088	00-04	179	283	16
Piave	ADR	Italy	1.33	00-05	0.020	03-05	780	1039	15
Pinios	AEG	Greece	2.09	00-02	0.703	00-02	69	144	49
Po	ADR	Italy	1.91	01-05	0.082	01-05	683	1302	56
Rhone	NWE	France	1.44	00-05	0.050	00-05	564	812	28
Strymon	AEG	Greece	1.39	00-04	0.222	00-04	157	218	35
Tagliamento	ADR	Italy	1.23	01-05	0.031	01-05	750	924	23
Tevere	TYR	Italy	2.10	03-04			446	937	
Turia	NWE	Spain	3.22	00-05	0.235	05	42	135	10
Vjose	ADR	Albania	1.04	01-05	0.018	01-05	917	951	16

Average concentrations were taken from EEA (2007), except data for the Danube (TNMN, 2002) and the Aude and Herault rivers (Ludwig et al. (2003). Long term average runoff values from Ludwig et al. (2003) were used for flux calculations (F-NO_3 and F-PO_4).

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 7 *– Average silica fluxes and concentrations of some world rivers included in the UNEP/ GEMS monitoring program*

		average drainage basin temperature		
	all	T ≤ 12 °C	T = 12-20 °C	T ≥ 20 °C
number of rivers	62	21	18	23
Q (mm)	355 ± 385	282 ± 167	265 ± 239	508 ± 551
Si flux (kg Si km^{-2} yr^{-1})	1368 ± 1834	690 ± 438	883 ± 973	2365 ± 2599
Si conc. (mg Si l^{-1})	3.9 ± 2.2	2.6 ± 1.3	3.9 ± 2.2	5.2 ± 2.2
R^2 (Q – Si flux)	0.85	0.41	0.78	0.89
R^2 (log Q – log Si flux)	0.78	0.62	0.80	0.87

±: standard deviations; average temperatures were determined from Mitchell and Jones (2005) according to the drainage basin delineations defined by Vörösmarty et al., 2000b.

ACCEPTED MANUSCRIPT

Table 8 – *Riverine nutrient budgets for the Mediterranean and Black Sea*

		ALB	SWE	NWE	TYR	ADR	ION	CEN	AEG	NLE	SLE	BLS	WMED	EMED	MED
Nitrogen (10^3 t N yr^{-1})	1963	2	9	44	18	74	8	4	36	16	12	903	72	151	223
	1968	3	15	80	27	119	13	6	60	27	8	1213	125	233	358
	1973	4	24	108	42	186	20	10	86	34	11	1282	178	346	524
	1978	6	30	155	60	272	28	14	124	55	17	1456	251	510	760
	1983	6	38	184	71	297	34	16	144	61	21	1410	299	573	872
	1988	9	42	199	79	321	36	19	162	72	25	1414	329	636	965
	1993	7	45	222	83	372	39	19	176	77	32	1227	357	716	1073
	1998	10	47	219	88	351	42	21	179	78	42	1116	364	713	1077
Phosphorus (10^3 t P yr^{-1})	1963	0.1	0.7	4.4	1.3	5.2	0.6	0.3	2.7	1.2	5.9	63.4	6.6	15.9	22.5
	1968	0.2	1.1	7.1	2.0	8.4	1.0	0.5	4.5	2.0	0.6	79.7	10.4	17.0	27.4
	1973	0.4	2.2	12.5	3.9	17.2	1.8	0.9	8.1	3.2	1.1	78.5	19.0	32.3	51.3
	1978	0.7	3.6	20.3	7.2	28.7	3.3	1.6	14.8	6.5	2.2	83.2	31.7	57.3	88.9
	1983	0.7	4.5	29.8	8.4	32.3	4.0	1.9	17.2	7.3	2.7	78.3	43.3	65.5	108.8
	1988	0.8	3.9	26.5	7.4	26.1	3.4	1.8	15.3	6.9	3.1	78.3	38.6	56.5	95.2
	1993	0.5	3.0	15.8	5.5	20.4	2.5	1.3	11.3	5.1	3.4	53.7	24.8	44.0	68.8
	1998	0.5	2.2	10.3	4.1	14.0	1.9	1.0	8.1	3.6	3.7	55.1	17.1	32.3	49.4
Silica (10^3 t Si yr^{-1})	1963	28	32	264	63	323	42	21	182	75	103	936	387	746	1133
	1968	25	35	255	55	336	44	15	186	95	15	1027	371	691	1061
	1973	21	49	232	73	335	46	17	169	54	12	817	375	635	1010
	1978	18	41	269	81	399	52	22	183	86	13	927	409	755	1164
	1983	7	33	244	64	311	45	18	154	69	11	839	348	608	956
	1988	12	28	229	56	280	33	17	127	62	12	789	325	530	855
	1993	8	26	240	54	321	37	17	143	67	13	758	328	597	924
	1998	16	30	254	68	325	48	17	179	79	11	861	369	659	1028
PPR (g C m^{-2} yr^{-1})*	1963	0.07	0.11	0.72	0.22	1.63	0.14	0.02	0.55	0.44	**0.16**	5.65	0.32	0.39	0.37
	1968	0.12	0.17	1.15	0.34	2.64	0.22	0.03	0.91	0.75	0.06	7.10	0.51	0.42	0.45
	1973	0.19	0.33	2.03	0.67	5.39	0.40	0.06	1.65	1.17	0.11	6.99	0.93	0.80	0.84
	1978	0.38	0.54	3.30	1.22	9.01	0.74	0.11	3.02	2.42	0.21	7.41	1.55	1.41	1.45
	1983	0.35	0.69	**4.14**	1.42	10.14	0.89	0.13	3.51	2.71	0.26	6.97	**2.02**	1.61	1.78
	1988	0.44	0.60	4.31	1.26	8.20	0.76	0.12	3.11	2.54	0.29	6.98	1.89	1.39	1.56
	1993	0.25	0.46	2.58	0.93	6.41	0.56	0.09	2.31	1.87	0.32	4.79	1.21	1.08	1.12
	1998	0.25	0.34	1.68	0.70	4.39	0.43	0.07	1.66	1.32	0.35	4.91	0.84	0.79	0.81

* Potential marine primary production supported by rivers. The values were calculated according to the limiting nutrient in the river loads (P = normal, N = bold) and averaged for 5 years time slices. For basin abbreviations, see Table 1.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

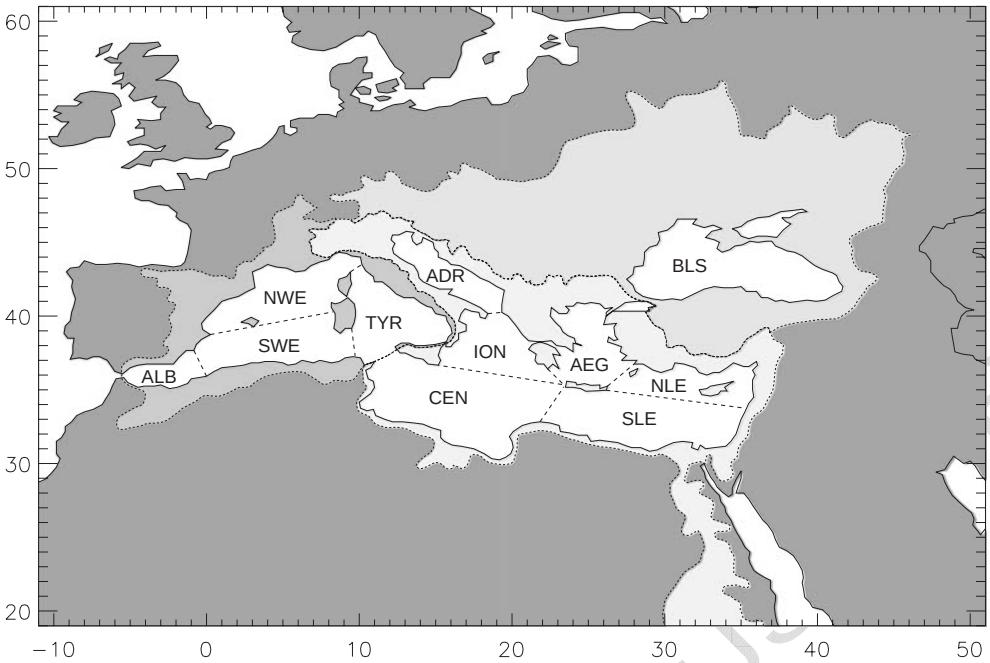


Figure 1 *– Drainage basins of the Western Mediterranean, the Eastern Mediterranean and of the Black Sea (different grey scales). Major sub-basins of the Mediterranean (Cruzado, 1985) are shown as well. For abbreviations, see Table 1.*

ACCEPTED MANUSCRIPT

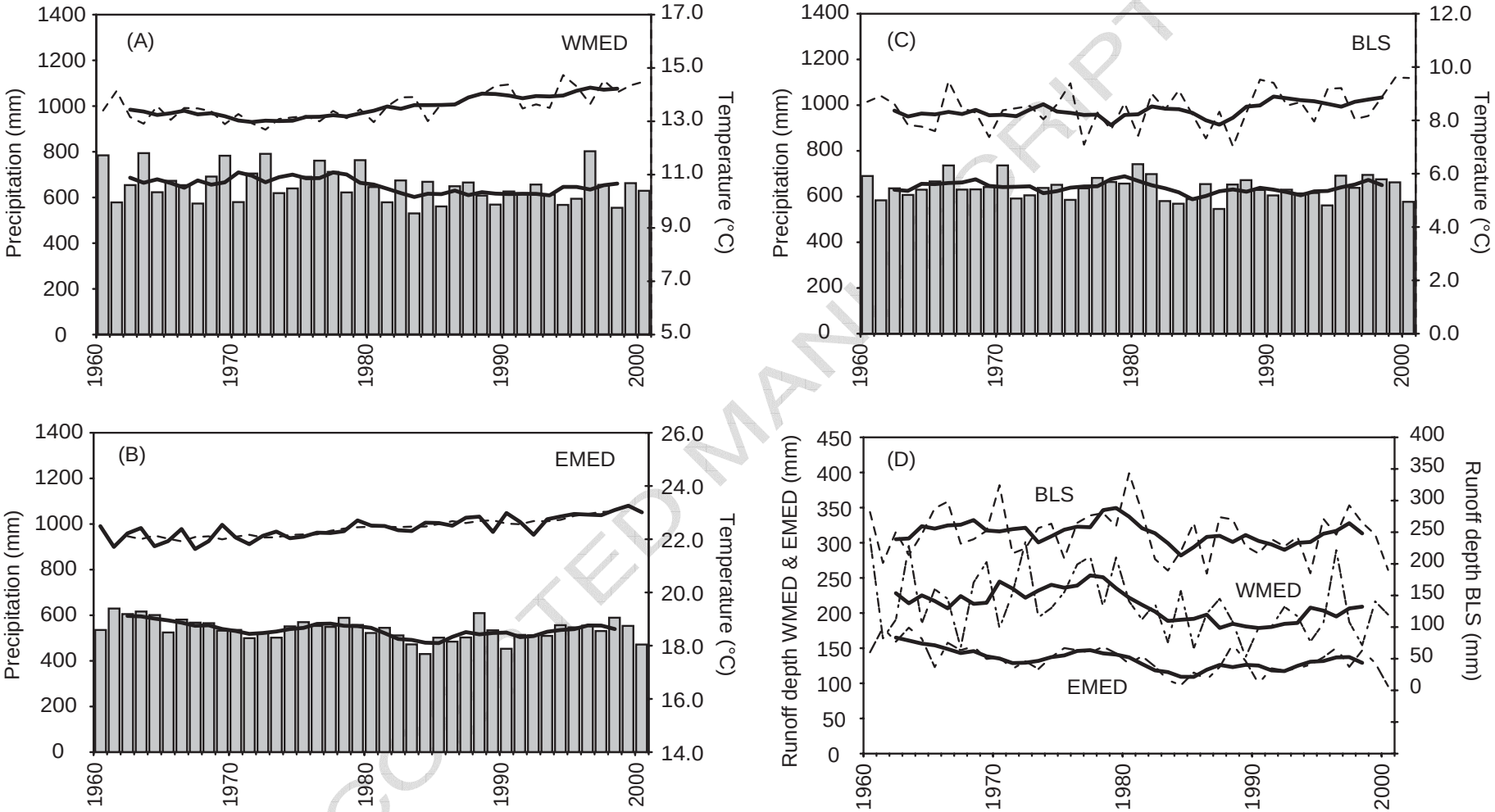


Figure 2 *– Evolutions of precipitation (grey bars) and temperature in the drainage basins of the Mediterranean and Black Sea. (**a**) Western Basin; (**b**) Eastern Basin; (**c**) Black Sea. (**d**) Evolutions of average runoff depth in the three basins according to Q-Pike (see text). Bold lines are 5 year running means.*

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

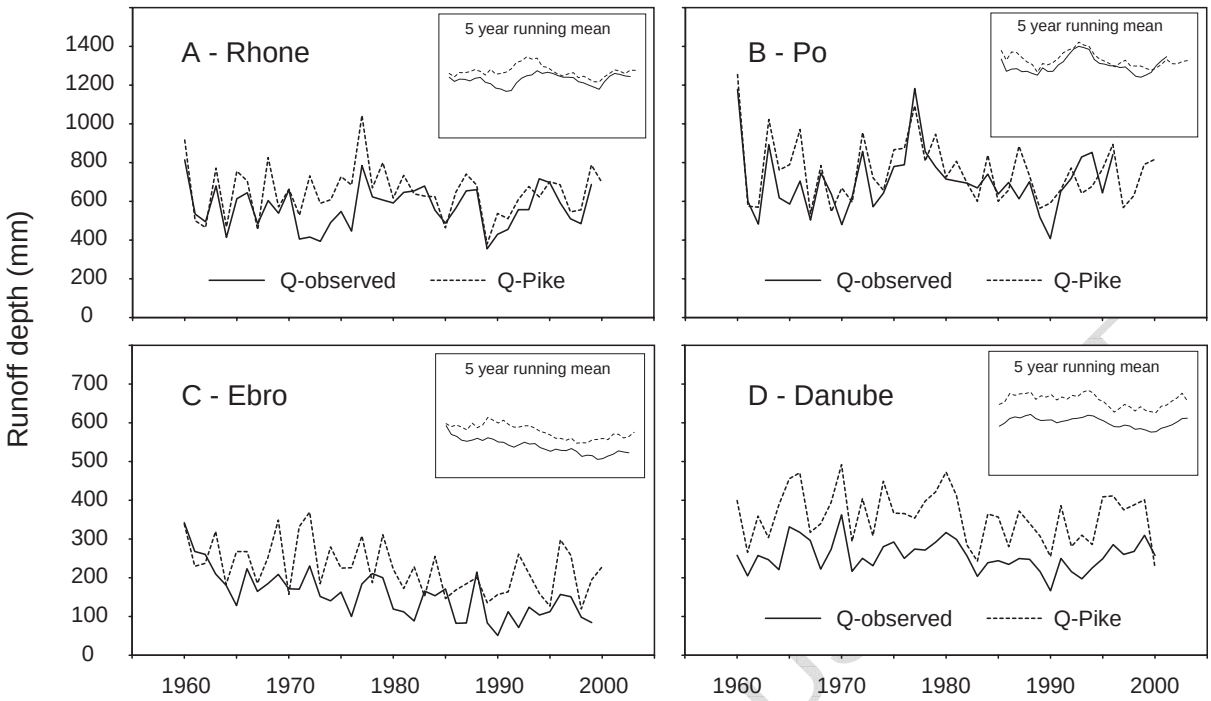


Figure 3 *– Comparison between observed and predicted (Q-Pike) runoff depths for the Rhone (**a**), the Po (**b**), the Ebro (**c**) and the Danube (**d**) rivers. For further explanation, see text.*

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

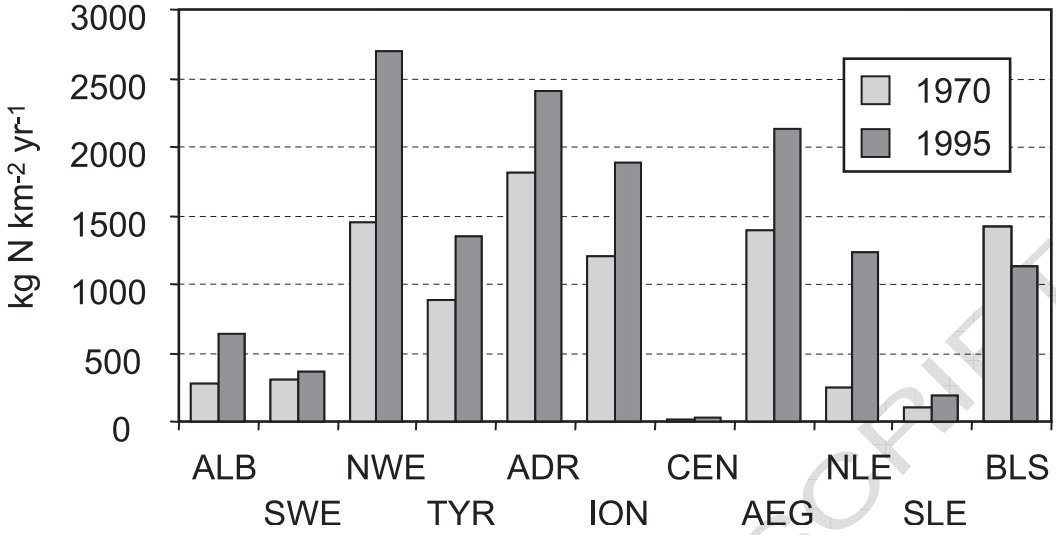


Figure 4 *– Fertilizer use in the different drainage basins of the Mediterranean and Black Seas in 1975 and 1995 (data source Bouwman et al., 2005); for basin abbreviations, see Table 1).*

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

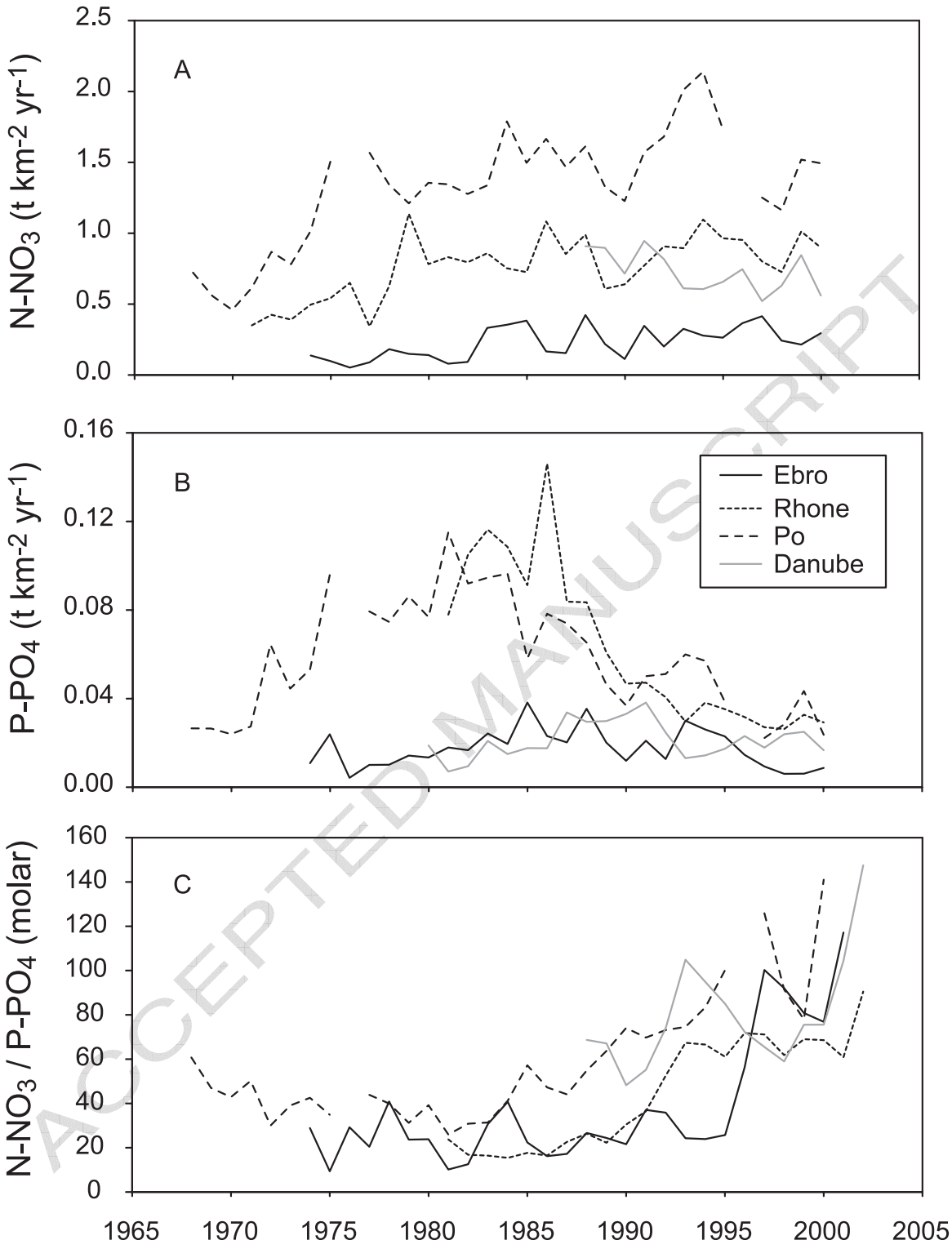


Figure 5 *– Long-term evolution of specific nutrient fluxes in the large Mediterranean and Black Sea rivers. (**a**) nitrate, (**b**) phosphate, (**c**) corresponding N/P ratio. Data for the Po, Rhone and Ebro rivers are from Ludwig et al., 2003. For the Danube, they are from Garnier et al. (2002a) for 1980 – 1995 and from TNMN (2002) for 1996 – 2002.*

ACCEPTED MANUSCRIPT

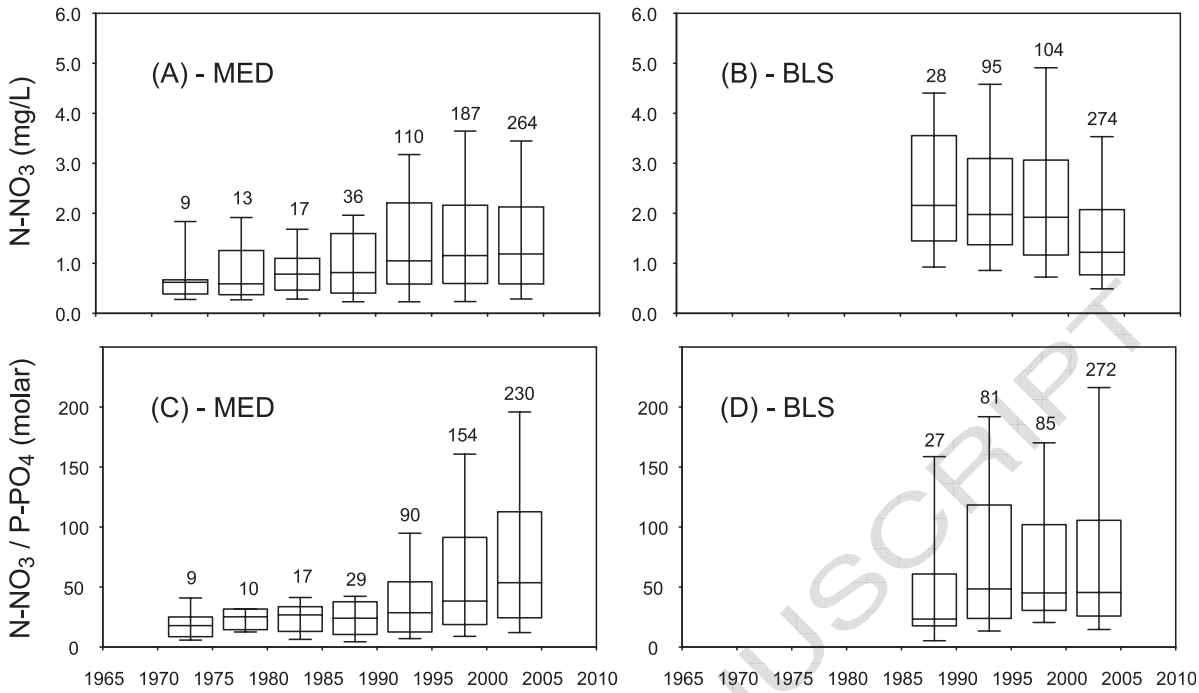


Figure 6 *– Box plot distributions (10, 25, 50, 75, 90 percentiles) of mean nutrient concentrations averaged for 5 years time slices. (a, b) nitrate in the rivers of the Mediterranean and Black Sea; (c, d) nitrate to phosphate ratios in these rivers. The values above the plots correspond to the number of different stations that were considered in the statistics. Data sources EEA (2007).*

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

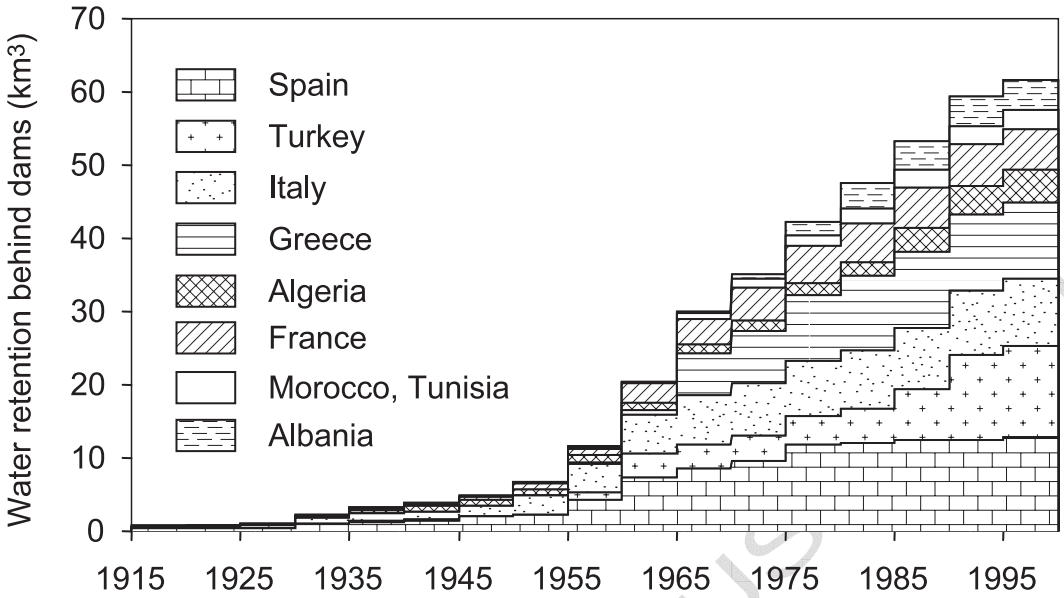


Figure 7 *– Evolution of the water retention behind dams in the drainage basin of the Mediterranean Sea. Adapted from Margat et Treyer (2004).*

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

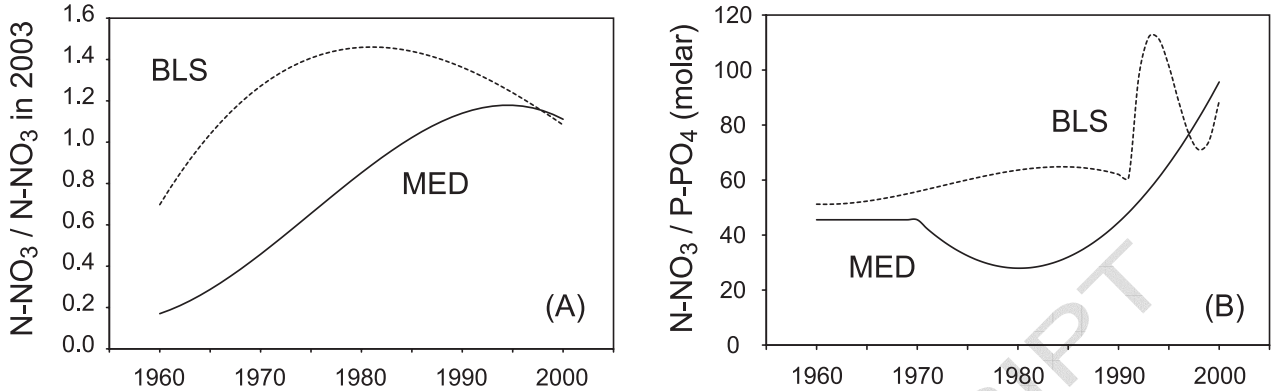


Figure 8 *– (**a**) Average evolutions of the nitrate supply to the Mediterranean and Black Sea by rivers, normalized to the fluxes in 2003; (**b**) average evolutions of the associated N-NO3/ P-PO4 ratios. For further explications, see text.*

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

	ALB	SWE	NWE	TYR	ADR	ION	CEN	AEG	NLE	SLE	BLS	WMED	EMED	MED
1960	P	P	P	P	P	P	P	P	P	N	P	P	P	P
-	P	P	P	P	P	P	P	P	P	N	P	P	N	P
-	P	P	P	P	P	P	P	P	P	N	P	P	P	P
-	P	P	P	P	P	P	P	P	P	N	P	P	P	P
-	P	P	P	P	P	P	P	P	P	N	Si	P	P	P
1965	P	P	P	P	P	P	P	P	P	P	Si	P	P	P
-	P	P	P	P	P	P	P	P	P	P	Si	P	P	P
-	P	P	P	P	P	P	P	P	P	P	Si	P	P	P
-	P	P	P	P	P	P	P	P	P	P	Si	P	P	P
-	P	P	P	P	P	P	P	P	P	P	Si	P	P	P
1970	P	P	P	P	P	P	P	P	P	P	Si	P	P	P
-	P	P	P	P	P	P	P	P	P	Si	Si	P	P	P
-	P	P	P	P	P	P	P	P	P	P	Si	P	P	P
-	P	P	P	P	P	P	P	P	P	P	Si	P	P	P
-	P	P	P	P	P	P	P	P	P	Si	Si	P	P	P
1975	P	P	N	P	Si	P	P	P	Si	Si	Si	P	P	P
-	P	P	P	Si	Si	P	P	P	Si	Si	Si	P	Si	P
-	P	Si	N	Si	P	P	P	Si	P	Si	Si	N	P	P
-	P	Si	Si	Si	P	P	P	Si	P	Si	Si	Si	Si	Si
-	P	Si	Si	Si	Si	P	Si	Si	Si	Si	Si	Si	Si	Si
1980	P	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	Si	Si	Si	Si	Si	Si	P	Si	Si	Si	Si	Si	Si	Si
-	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
1985	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	P	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	P	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	P	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
1990	P	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	P	Si	P	Si	P	Si	Si	Si	Si	Si	Si	Si	Si	Si
-	P	Si	P	Si	P	Si	Si	Si	Si	Si	P	Si	Si	Si
-	P	Si	P	Si	P	P	P	P	P	Si	P	P	P	P
1995	P	Si	P	Si	P	P	P	P	P	Si	P	P	P	P
-	P	Si	P	Si	P	P	Si	P	P	Si	P	P	P	P
-	P	Si	P	P	P	P	P	P	P	Si	P	P	P	P
-	P	P	P	P	P	P	P	P	P	Si	Si	P	P	P
-	P	P	P	P	P	P	P	P	P	Si	P	P	P	P
2000	P	P	P	P	P	P	P	P	P	Si	P	P	P	P

Figure 9 *– Spatial and temporal variability of the limiting elements for marine diatom production that could be supported by rivers in the Mediterranean and Black Sea. For basin abbreviations, see Table 1.*

ACCEPTED