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RIVERINE TRANSPORT OF WATER, SEDIMENTS AND POLLUTANTS TO THE MEDITERRANEAN SEA

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- Curbing Pollution
- Safeguarding Natural and Cultural Resources
- Managing Coastal Areas
- Integrating the Environment and Development

TABLE OF CONTENTS

List of tables

Page

List of figures

Summary

A – General purpose

The present report is based on a data collection on Mediterranean rivers that has been started in 1997 and updated in 2002. It focuses on the riverine transport of water, sediments, and pollutants to the Mediterranean Sea. The major objectives were (i) to dress a detailed picture of the spatial variability of the pollution state in comparison with other world rivers, and (ii) to reconstruct the evolution of water quality during the recent decades. As far as possible, budgets should be given allowing the identification of the major sources of the riverine matter in terms of regions and countries, as well as the identification of the relative contribution of the riverine inputs to the different Mediterranean sub-basins.

The report is organised in seven major chapters. After (i) a general introduction to the hydroclimatic, morphological and socio-economical particularities of the Mediterranean drainage basin, the following chapters deal with (ii) the water and (iii) sediment fluxes, (iv) the organic matter pollution, (v) the nutrient fluxes, (vi) the heavy metal pollution and finally pesticides and persistent organic chemicals. For all of these topics, a great number of data on different Mediterranean rivers are presented and discussed in detail. More than 70 rivers were included in this report. However, the spatial distribution of these rivers is not entirely representative for the Mediterranean area, since the data availability is biased towards the rivers of the northern countries. In general, the data availability is sufficient for the French, Italian, Spanish and Greek rivers, whereas the data are less abundant, for example, for the Croatian, Albanian, Turkish and/ or North-African rivers.

The most complete data records can be found for the large northern rivers, which are the Po, Rhone and Ebro rivers. For many of the investigated parameters, we present data records covering the last 30 years, allowing the tracking of the their temporal evolution and the identification of most recent trends. These trends could often be confirmed by the data on other rivers, indicating that these trends may be extrapolated to larger scales. The pollution state of rivers can evolve rapidly and an assessment cannot be done without mentioning the corresponding reference period. Trend analyses therefore took an important place in our study.

B – Major findings

Mediterranean particularities - An assessment of the environmental state of the rivers in the Mediterranean area cannot be understood without taking into account the particularities of this region. This concerns mainly the strong variability of the water discharge, and the strong anthropogenic pressure on the water resources. The first point is important because of the often extreme draughts in summer, average pollution loads may more easily cause environmental damage than in rivers of other climates with a more regular water flow. Regular monitoring of water quality is also more difficult under these conditions because it requires higher sampling frequencies. The second point translates the fact that the rivers are highly affected by artificial river damming and anthropogenic water extraction. In the Ebro River alone, more that 180 reservoirs have been constructed. It is evident that this can have a strong impact on the natural functioning of the river systems, and may increase their vulnerability for environmental harm.

Water discharge – Water discharge plays a key role in the transport of riverine matter to the sea. Even if the average concentrations of different pollutants can be determined with reasonably good precision, flux estimates can only be as good as the estimates for the corresponding water discharges. We reconstructed the evolution of riverine runoff to the Mediterranean up to the beginning of the last century in order to evidence the major changes that may have occurred. It is probably for the first time that water riverine budgets for the entire Mediterranean Sea have been determined with such detail. It can be shown that there occurred a continuous decrease in water discharge because of both climate change and anthropogenic water use. Actual water discharge to the entire Mediterranean Sea was estimated to about 330 km^3/yr, which is only 55% of what it has been at the beginning of the 20th century. The decrease especially accentuated after the 1970s, with strongest reductions in the Alboran and Aegean Sea. Only for the Rhone and the Po rivers, the two largest river basins, the average runoff seems to remain at constant levels, which means that their relative importance in the overall water supply to the Mediterranean Sea may have considerably increased.

Sediment fluxes – Sediment fluxes are the second key parameter controlling the riverine transfer of terrestrial matter to the sea. Because of the strong seasonality of climate, the presence of elevated mountain ranges, the wide dominance of younger, softer rocks, and a long history of human activity, Mediterranean rivers tend to have very high values of natural sediment fluxes. We estimate that the natural sediment supply to the Mediterranean Sea may have been in the range of 730 Mt/yr, corresponding to average sediment yield of about 580 t/km^2/yr. Because of the massive constructions of reservoirs, however, the actual sediment flux may be less than 200 Mt/yr. These figures are based on general extrapolations and they are associated with considerable uncertainty. Their refinement would require the development of sophisticated modelling tools, which is beyond the scope of this study. A major problem in the evaluation of sediment fluxes is the extreme temporal variability of the fluxes in the Mediterranean climate. The sampling frequency of classical monitoring programs on water quality does not allow the determination of reliable sediment fluxes, which also means that the evaluation of the fluxes of particulate pollutants is not possible unless this is changed.

Organic and bacteriological pollution – Organic pollution seems to be a greater problem in the rivers of the Mediterranean countries than in the rivers of the northern European countries. It is normally related to effluents from point sources such as household or industry wastewater. Also bacterial pollution is often originating from the same sources, although wastewater from agriculture may also be a major source for this pollution type. The extent to which these wastewaters are discharged into surface waters naturally depends on the wastewater treatment facilities available. Sewage plants are expensive, and money is more seriously missing in the southern than in the northern countries. Nevertheless, also in southern Europe, the treatment of municipal and industrial wastewater has significantly improved during the past 10 to 15 years, even if this evolution was less rapid than in the north European countries. Good examples are the Rhone and the Po rivers, where the BOD loads depict a three to fivefold reduction over the 1980 -1990 period, respectively. In the Ebro River, however, the loads rather tend to increase towards recent years, showing that wastewater treatment is not improved everywhere to the same extent.

However, the contributions of organic rich wastewater loads do not necessarily lead to elevated organic matter contents in the Mediterranean rivers. Dissolved organic carbon (DOC) concentrations are quite low compared to other world rivers, which can be explained by the steep morphologies, the often-low drainage intensities and the carbon poor soils in the Mediterranean area. DOC largely reflects the organic compounds origination from the leaching of soil organic matter, which are chemically rather inert and which are not necessarily available for rapid biological decomposition in the river waters.

Nutrients – In our assessment on nutrients, we mainly focussed on the levels of dissolved nitrate, dissolved phosphate and total phosphorous. The latter can strongly be controlled by the fluxes of particulate matter, for which the data availability is often insufficient to determine reliable averages. We normally assumed that the evolution of total phosphorous entirely followed the evolution of phosphate, although this has, of course, not necessarily to be the case.

In general, nutrient pollution is moderate in the Mediterranean rivers compared to the rivers of northwestern Europe and/ or North America, reflecting the general land use practises and population densities in the Mediterranean countries. Fertiliser application, for example, is less intense in the south than in the north. This is true for all nutrient forms, but spatially the patterns of nitrogen and phosphorous pollution do not closely match, since both nutrients do not have the same origins. Nitrate loads are normally dominated by diffuse pollution from agricultural sources, whereas phosphorous compounds depend more closely upon point sources, mainly municipal sewage discharge. As a consequence, highest nitrate concentrations are found in rivers characterised by intense agricultural land use in the drainage basins, such as the Po River in Italy. Highest phosphate levels are typical for the rivers suffering from pollution due to urban wastewater inputs, such as the Besos River in Spain who receives the municipal effluents of Barcelona.

Also the temporal evolutions of the nitrate and phosphate loads in the Mediterranean rivers are different. For nitrate, the overall riverine input to the Mediterranean Sea increased continuously. It may almost have doubled from about 330 ktN/yr for <1975 to about 600 ktN/yr for >1995, even if during most recent years, the increase seems to slow down. Also phosphate loads strongly increased from about 15 ktP/yr for <1975 to about 40 ktP/yr for 1985-1990, but then dropped down to about the initial values as a result of the widely applied ban of phosphorous detergents and the general improvement of wastewater treatment facilities. The start of this decrease is not uniform in the different rivers, but the improvement is a widespread phenomenon.

Heavy metals – Because of the strong affinity of heavy metals to the solid phases in river water, the pollution state can be assessed best when looking at the heavy metal concentrations in the total suspended solids (in mg/kg). Our values witness a general impact of pollution in the Mediterranean rivers, especially for Hg, Cd, and Pb. However, when compared to the levels in the Seine or the Rhine rivers, one notes that the heavy metal concentrations are often two or three times lower in the Mediterranean rivers. Pollution is therefore less important compared to the river basins in north-western Europe, in agreement with the lower industrial development in the Mediterranean countries. It is also possible that, because of the high natural sediment yields (see above), dilution of urban and industrial sources by high levels of suspended solids may also contribute to the lower heavy metal contents.

Trends for the temporal evolution of the pollution levels are difficult to establish for heavy metals because of the lack of high quality data. Many monitoring programs only measure total metals without filtering the samples, although the utility of this information is restricted. On the other hand, one has to point out that the contamination problem is still a major problem for the analysis of heavy metals.

C – Recommendations

I - A permanent register of river quality data should be set up for rivers discharging to the Mediterranean Sea, as this already exists for European rivers (EEA - Eurowaternet) or at the global scale (GEMS-water). Such a register should especially focus on the integration of rivers from the countries for which actually only little information is available. This mainly concerns the rivers of the North-African countries, such as the Nile River, Turkish rivers, and the rivers of Croatia and Albania. Simple socio-economical attributes related to the land use and the water management practises (population density, industrial indices, wastewater treatment facilities, major reservoirs, etc.) should be associated to the water quality data. As far as possible, the analytical protocols should be standardised.

II – The monitoring programs should be specifically adapted to the hydrological regimes in the Mediterranean climate. The variability of water discharge is much higher in the Mediterranean rivers than for most other world rivers, which may cause problems for the calculation of representative pollution loads when only a few measurements are available. But the major problem naturally concerns the determination of reliable fluxes for total suspended solids. Almost all of the transport occurs during often brief and violent floods, which are difficult to be monitored by classical sampling. The calculation of reliable fluxes seems to be almost impossible unless automatic sampling and/ or other automatic monitoring devices have been installed. This is important because many pollutants in rivers are rather associated to the particulate than to the dissolved phases. Without knowing the corresponding sediment fluxes, it is very difficult to estimate, for example, average loads for total phosphorous and/ or heavy metals.

III – In the Mediterranean region there still exists a certain number of rivers that are only weakly polluted. It seems to be urgent to identify the few small river basins that are still in a near-pristine state in order to ensure the conservation of these typical Mediterranean rivers. The Krka and Neretva in Croatia, and/or the Var, Argens or Tavignano in France are examples for such basins. The protection of these rivers not only represents a public interest in terms of environmental resources, but also from a scientific standpoint, since studying these rivers may help to assess the impact of climate change and other global phenomenon on the natural functioning of river drainage basins.

Chapter I - Particularities of the Mediterranean basin

1.1 - Geography and Climate

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, which are shown in figure 1.1 and listed in table 1.1. The length of the Mediterranean coastline totals about 46 000 km, of which 19 000 km represent islands coastlines (Selenica, unpubl.). The entire coastal region covers an area of nearly 1.5 million km^2, 17% of the total area of the bordering countries: Spain, France, Monaco, Italy, Slovenia, Croatia, Bosnia, Serbia and Montenegro, Albania, Greece, Turkey, Cyprus, Syria, Lebanon, Palestinian Territories, Israel, Egypt, Libya, Malta, Tunisia, Algeria, and Morocco.

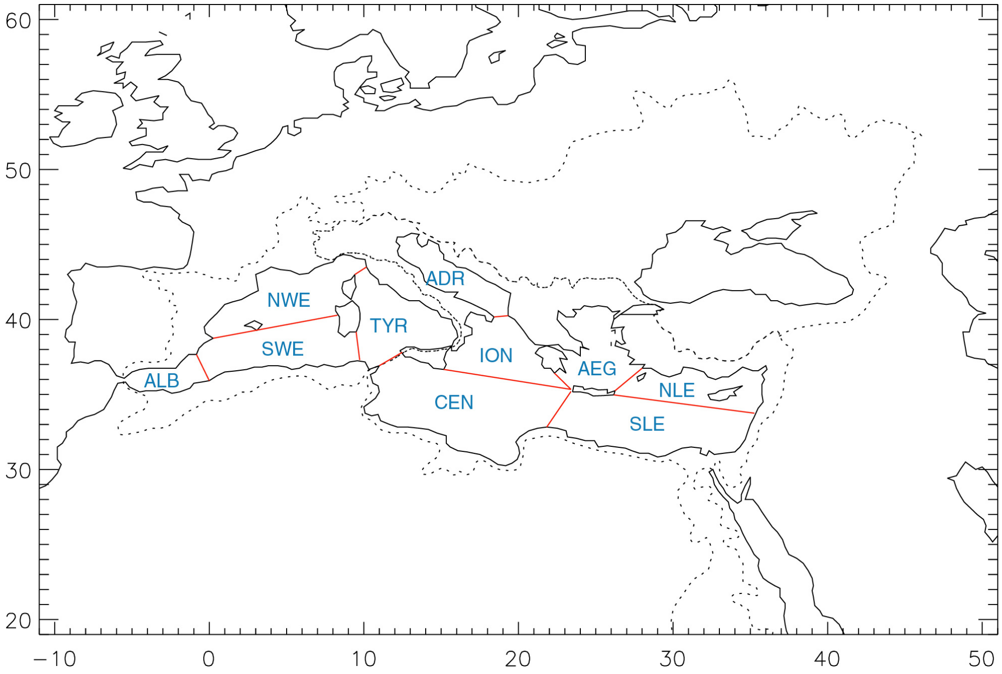

Fig. 1.1 *- Major sub-basins of the Mediterranean Sea. The dashed lines show the drainage basins of the western basin, the eastern basin, and the Black Sea, respectively. For abbreviations, see table 1.1*

Climatically, the Mediterranean is characterised by generally warm temperatures, winter-dominated rainfall, dry summers and a profusion of microclimates due to local environmental conditions. Mean annual temperature follows a marked north to south gradient to which local orographic effects are superimposed (fig. 1.2a). Lowest temperatures of <5 °C can be found in the higher parts of the Alps, whereas temperatures of >20 °C are typical for Libya or Egypt. Also mean annual precipitation shows a north to south gradient, with decreasing values towards the south. But orography is naturally the dominant factor here (fig. 1.2b). High precipitation values of 1500-2000 mm and more are found in the alpine and Pyrenean headwater regions of the Po, the Rhone and the Ebro rivers, and they are very abundant in the alpine mountain belt bordering the Dalmatian coast, from the Istrian peninsula down to Albania. This makes these countries to the most humid countries of the Mediterranean area.

The strong summer-winter rainfall contrast is one of the major characteristics of the Mediterranean climate. This contrast is more and more pronounced when going from the north to the south and from the west to the east (fig. 1.2c and 1.3a-d). Precipitation mainly falls during winter and autumn (fig. 1.3a, d) whereas summer is very dry. Often, less than 10% of the annual precipitation falls during this period (fig. 1.3c). This contrasts starkly with the continental climate in the drainage basin of the Black Sea, where most of the precipitation occurs during summer. During spring, the rainfall contribution to the mean annual precipitation is quite homogenous in the entire Mediterranean region (fig. 1.3b). High precipitation during autumn is typical for the coasts of Spain, France, Italy, Croatia, Serbia and Montenegro, Albania and Greece. Further east, such as in Turkey and in Lebanon, autumn precipitation is much less important. By far most of the rainfall occurs here in winter.

Table 1.1 *- Major sub-basin of the Mediterranean Sea*

Basin	Code	Bordering countries
Alboran	ALB	Spain, Morocco, Algeria
North-Western	NWE	Spain, France, Monaco, Italy
South-Western	SWE	Spain, Italy, Algeria, Tunisia
Tyrrhenian	TYR	Italy, France, Tunisia
Adriatic	ADR	Italy, Croatia, Albanian
Ionian	ION	Italy, Albanian, Greece
Central	CEN	Italy, Tunisia, Libya, Malta
Aegean	AEG	Greece, Turkey
North-Levantine	NLE	Turkey, Cyprus, Syria, Lebanon
South-Levantine	SLE	Lebanon, Israel, Egypt, Libya

In certain regions, precipitation especially in autumn can occur in the form of heavy downpours, leading to violent flash floods in the rivers of these regions. The prevalent zones for flash floods are the Côte d’Azur, east Pyrenees, Cevennes and Corsica in France, the northwestern areas of Italy, and Catalonia and Valencia in Spain (Estrela et al., 2001).

One result of the seasonal rainfall and high evaporation is that water shortages are endemic. The problem is particularly striking in the southern parts of the Mediterranean in contrast to seasonal shortages in the north (corresponding to the dry months). The dry season in some southern countries exceeds six months, meaning that water shortage is a permanent handicap for sociological and economic development.

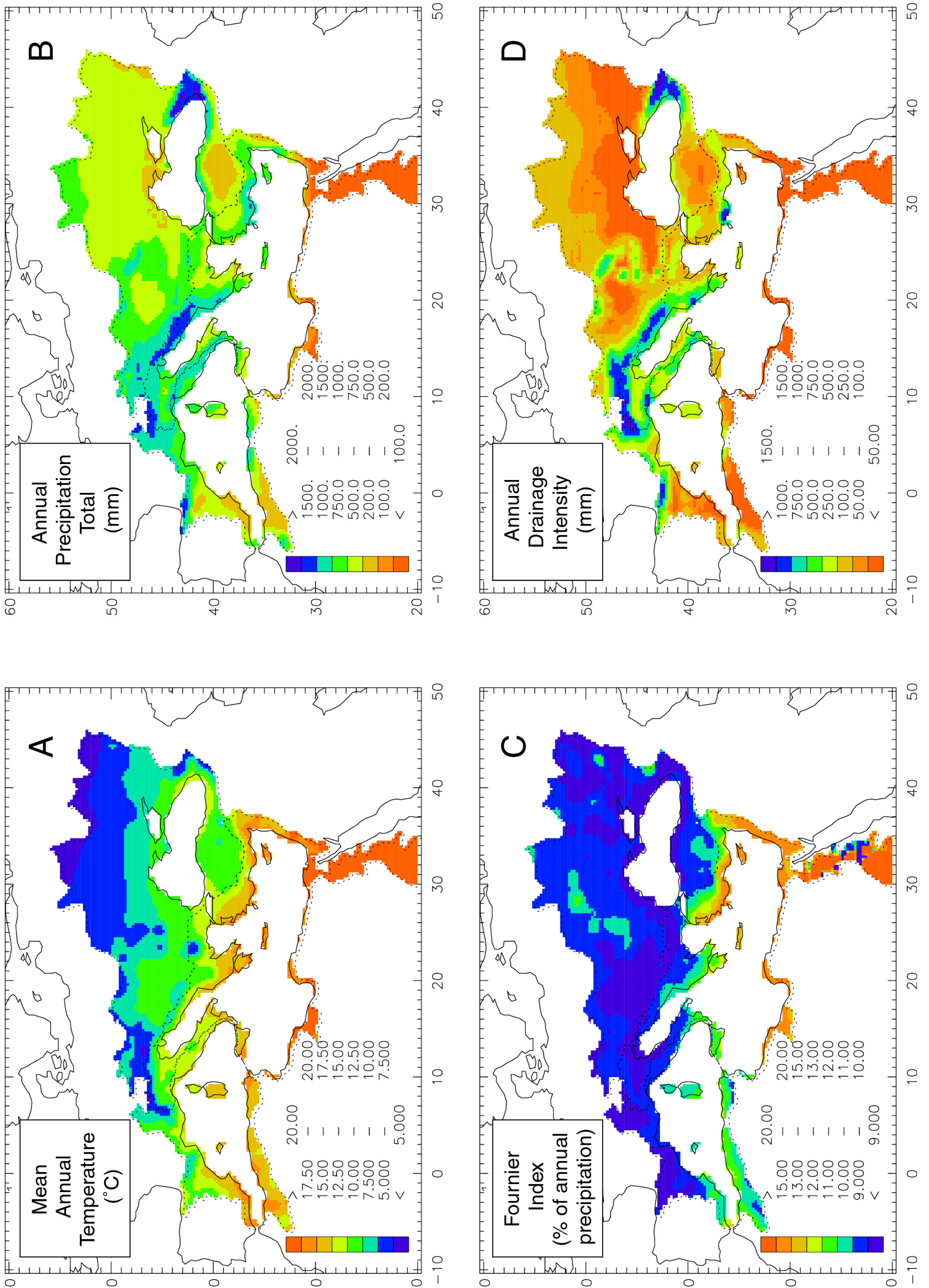

Fig. 1.2a-d *- Climatic patterns of the Mediterranean and Black Sea drainage basins. A - Mean annual temperature (Legates and Willmott, 1992); B - Annual precipitation total (Korzoun et al., 1977); C - Fournier index (= sum of the square of monthly precipitation over annual precipitation; CORINE, 1992) D - Drainage intensity (Korzoun et al., 1977).*

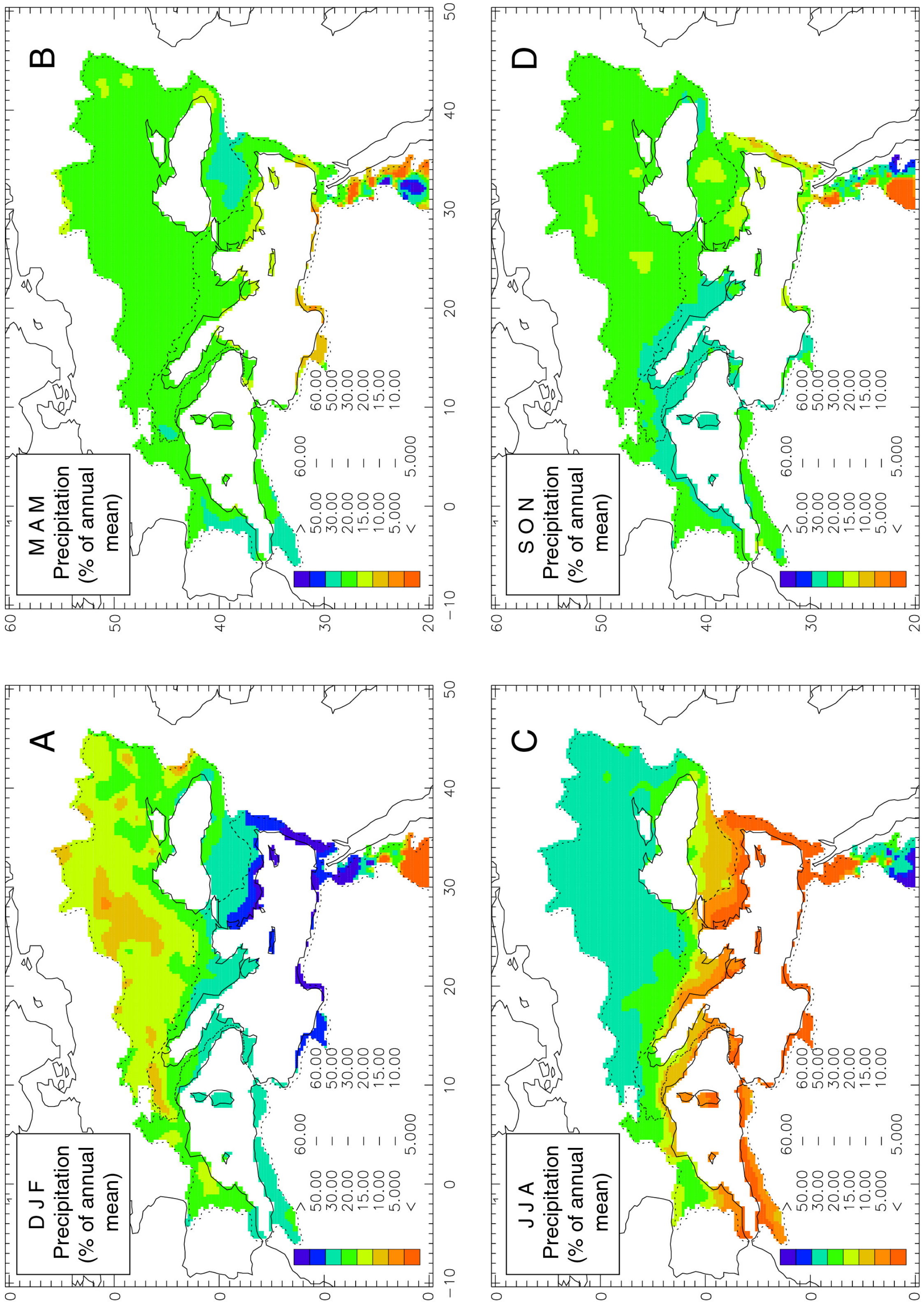

Fig. 1.3a-d *- Seasonal variability of precipitation in the Mediterranean and Black Sea drainage basins according to Legates and Willmott (1992). A - Winter (December, January, February); B - Spring (March, April, May); C - Summer (June, July, August); D - Autumn (September, October, November).*

1.2 - Population and Development

In 2000 the countries bordering the Mediterranean Sea had a combined population of about 430 million people (tab. 1.2). A considerable part of them live directly in the coastal zone. Especially in the southern countries, population densities are much greater in coastal than in non-coastal areas. Coastal population densities range from more than 1000/km^2 in the Nile Delta to less than 20/km^2 along coastal Libya (fig. 1.4). According to some projections, the population in the Mediterranean is expected to reach about 520 million in 2025 (Attané and Courbage, 2001). Increasingly the population will urbanise and it is expected that by the year 2025 about 75% of the population will be urban. The economic and environmental burden on cities, therefore, will increase substantially.

Table 1.2 *- Population density and development in the Mediterranean countries (from Attané and Courbage, 2001)*

		POPULATION			DENSITY	
COUNTRY	AREA	2000	2025	Trend	Total	* Med/ Tot
	(km^2)	(Thousand inhabitants)		(%)	(inhab./ km^2)	
SPAIN	504 783	39 815	40 769	+ 2.4	78	2.13
FRANCE	547 026	59 412	64 177	+ 8.0	103	1.20
ITALY	301 277	57 456	53 925	- 6.1	190	1.04
MALTA	316	389	430	+ 10.5	1145	1.00
MONACO	2	34	41	+ 20.6	15000	1.00
SLOVENIA	20 251	1 965	2 029	+ 3.3	100	0.57
CROATIA	56 538	4 473	4 193	- 6.3	87	0.68
BOSNIA-HERZEGOVINA	51 129	3 972	4 324	+ 8.9	87	0.58
SERBIA-MONTENEGRO	102 000	10 856	12 217	+ 12.5	104	0.55
ALBANIA	28 748	3 114	3 820	+ 22.7	113	1.29
GREECE	131 944	10 558	10 393	- 1.6	78	1.18
TURKEY	779 452	65 627	87 303	+ 33.0	72	1.28
CYPRUS	9 251				54	1.00
SYRIA	185 180	15 936	24 003	+ 50.6	77	4.23
LEBANON	10 230	3 206	4 147	+ 29.4	293	1.88
ISRAEL	20 770	5 851	7 861	+ 34.4	263	2.98
PALESTINIAN AUTHORITY	6 165	3 150	6 072	+ 92.8	365	6.33
EGYPT	997 739	66 007	94 895	+ 43.8	59	3.54
LIBYA	1 759 500	6 038	8 832	+ 46.3	3	8.28
TUNISIA	154 530	9 615	12 892	+ 34.1	57	2.37
ALGERIA	2 381 741	30 332	42 329	+ 39.6	10	22.21
MOROCCO	710 850	28 505	38 174	+ 33.9	37	2.39
TOTAL	8 759 422	426 311	522 826			

* ratio of the population density on the Mediterranean part of the country over the population density in the entire country

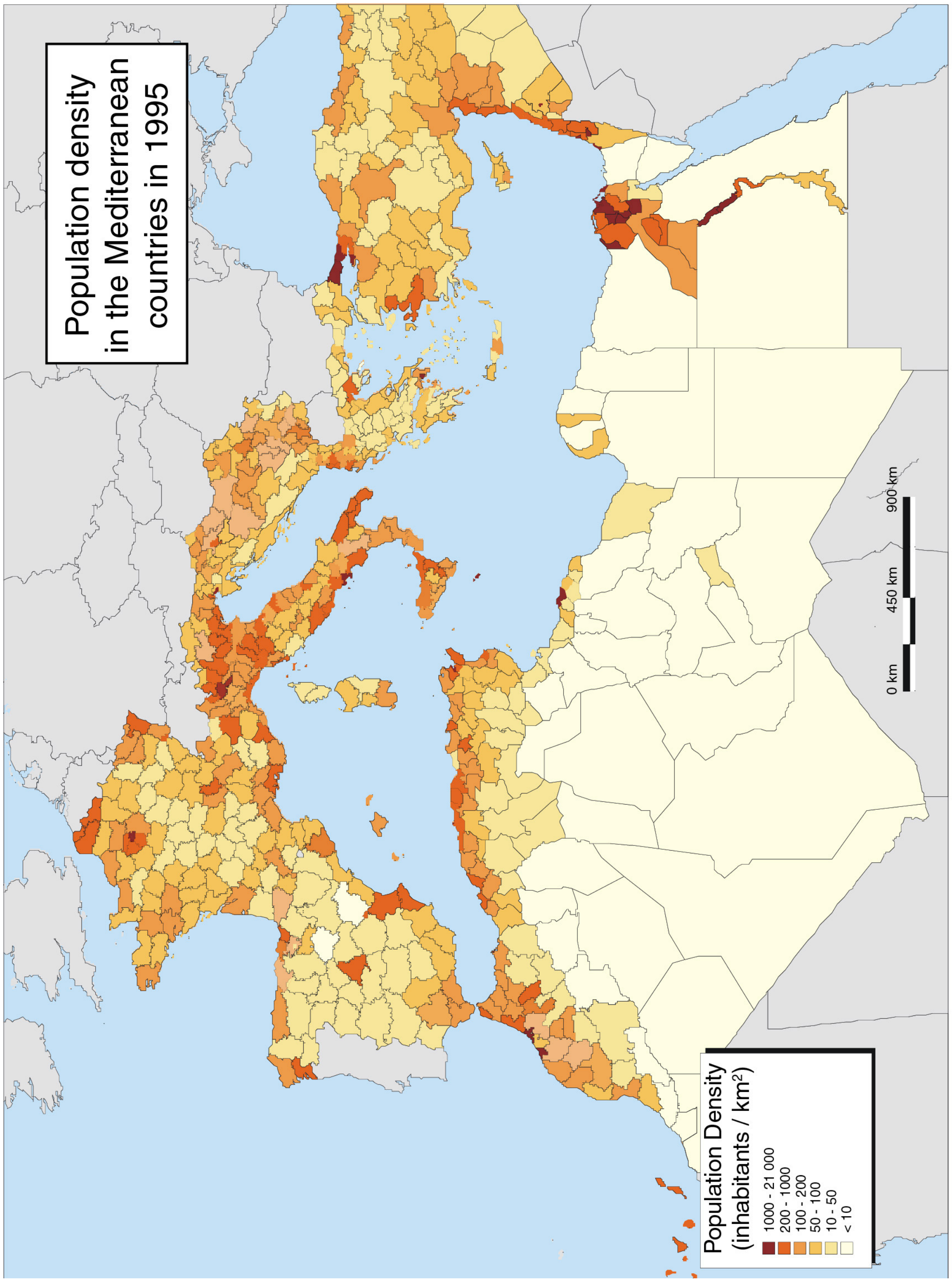

Fig. 1.4 - *Population density in the Mediterranean countries in 1995 (from PNUE, 2001)*

Population growth, however, shows major differences between north and south. The European countries have nearly stable population (tab. 1.2). In contrast, population growth in southern countries ranges from 2 to 3% per year. As a result the population in the coming years will increase and became younger in the south. With this shift will come increasing problems concerning education and job-creation in southern countries. The wide variation in political and economic systems as well as historic differences have led to great discrepancies in the level of development between Mediterranean countries. The highly developed industrial countries in the north (France, Italy and Spain) and countries on the way to become industrialised (Greece, Serbia and Montenegro and Turkey) stand in stark contrast to the countries in the south.

1.3 - Resources

Mediterranean countries mostly lack natural resources. Libya, Algeria and Egypt are considered moderate-sized petroleum producers, Morocco is the world's third-largest producer of phosphates, Albania the third largest producer of chrome, and Spain the second largest producer of mercury (Selenica, unpubl.). Water resources are relatively plentiful in the North but scarce in the south. Forests have limited economic significance, but are important for the preservation of soil as for recreation and landscape.

Mediterranean agriculture is characterised by multi-faceted crops, particularly olives, citrus fruits, grapes and hard grain; the main livestock is sheep. Increasingly, irrigation is needed in the south to maintain or increase crop production. While coastal regions tend to have little agricultural land, it often is of high quality, particularly around delta areas. However, Mediterranean agriculture is also characterised by long-term misuse and overexploitation. In part this is due to generally poor soils, lack of rain and the increasing population pressure (particularly in the south).

In recent years, efficient farming and growing urbanisation in the north has lead to increased abandonment of farmland and rangeland and the corresponding advance of forests. This contrast strongly in the South and east where marginal areas, such as arid steppes and rangelands, are being cleared for grain production; unfortunately, the lack of water resources and especially continually flowing rivers has restricted the use of irrigation. One result has been the increased desertification in North Africa and the Near East. Given the trends of the past 40 years, in the near future virtually all tillable land in the southern and eastern part of the Mediterranean basin will be cultivated for cereal production, even through the risk will be high and the yields low.

Although alluvial and coastal plains are few and not extensive (the Nile Delta being far the largest) most coastal plains have demographic and economic importance ranging from agriculture to industry/ commerce to recreation to historical/archeological significance. Most areas still contain partly to little-modified natural ecosystems of irreplaceable value. Because of their ecological fragility, related to the land-use transition, and their economic importance, these coastal lowlands are particularly vulnerable to climatic changes that can affect hydrology, sea-level rise and ecosystems. Anthropogenic activities can also affect these areas because of pollution and sediments flows from upstream catchments.

Finally, it should be pointed out that because of both climate and historical/archeological significance, the Mediterranean continues to be the greatest tourist destination in the entire world. Conversely, tourism is the greatest consumer/user of the Mediterranean coast and the number of tourists continues increasing. Such a growth will mean an increasing demand for coastal space as well as such necessities as electric power and water. Furthermore, the impact on certain habitats (particularly sandy beaches and dunes) will increase.

1.4 - Mediterranean rivers

1.4.1 - Inventory of major rivers

Making an inventory of Mediterranean rivers is not an easy task. Many of them are small rivers. The often-steep relief in the northern part of the drainage basin is in favour of the formation of small coastal rivers with relative short distance between the headwaters and the river mouths. In the south, the hydrographic network is often badly organised (archaic), such as in Libya, Egypt, Israel, Lebanon and/ or Syria, where the hot and dry climate does not allow the formation of larger river systems.

Table 1.3 *- Major rivers discharging into the Mediterranean Sea*

Sub-basin	River	Country	River mouth Lat.	Long.	Area 10^3 km^2	Area source	Q-actual km^3/yr	(mm)	Discharge source
ALB	MOULOUYA	Morocco	35.08	-2.42	51.0	*92.009*	1.58	31	*92.009*
ALB	MARTIL	Morocco	35.58	-5.32					
ALB	GUADALHORCE	Spain	36.68	-4.45	2.9	*76.133*	0.27	95	*76.133*
SWE	ISSER	Algeria	36.87	3.80	31.6	*84.209*	6.12	194	*84.209*
SWE	CHELIFF	Algeria	36.02	0.12	43.7	*84.211*	1.26	29	*84.211*
SWE	SOUMMAM	Algeria	36.75	5.07	8.0	*77.142*	0.79	99	*77.142*
SWE	SEYBOUSSE	Algeria	36.92	7.78	6.0	*77.142*	0.41	68	*77.142*
SWE	TAFNA	Algeria	35.28	-1.50	6.9	*95.013*	0.28	41	*95.013*
SWE	KEBIR	Algeria	36.83	6.12	1.1	*95.013*	0.23	209	*95.013*
SWE	SEGURA	Spain	38.08	-0.65	14.9	*76.126*	0.04	3	*97.004*
NWE	RHONE	France	43.92	4.67	95.6	*84.211*	53.90	564	*01.001*
NWE	VAR	France	43.65	7.20	1.8	*76.126*	1.57	858	*97.005*
NWE	AUDE	France	43.22	3.23	4.6	*97.005*	1.31	283	*97.005*
NWE	HERAULT	France	43.28	3.43	2.6	*97.005*	0.92	354	*97.005*
NWE	ORB	France	43.25	3.30	1.8	*95.013*	0.86	478	*97.005*
NWE	TET	France	42.73	3.03	1.4	*97.005*	0.40	291	*97.005*
NWE	ARGENS	France	43.40	6.73	2.6	*97.005*	0.38	146	*97.005*
NWE	ARNO	Italy	43.68	10.28	8.2	*97.007*	2.10	255	*91.081*
NWE	EBRO	Spain	40.82	0.52	84.0	*84.211*	9.24	110	*97.004*
NWE	JUCAR	Spain	39.12	-0.65	21.6	*84.211*	1.26	58	*97.004*
NWE	TER	Spain	42.02	3.20	3.0	*95.058*	0.84	279	*95.058*
NWE	LLOBREGAT	Spain	41.32	2.15	4.9	*78.162*	0.47	95	*97.004*
NWE	FLUVIA	Spain	42.20	3.12	0.8	*76.133*	0.36	360	*97.010*
NWE	TURIA	Spain	39.45	-0.32	6.4	*78.162*	0.27	42	*97.004*
NWE	MIJARES	Spain	39.92	-0.02	2.5	*97.004*	0.20	79	*97.004*
NWE	BESOS	Spain	41.42	2.07	1.0		0.13	126	*97.010*

Table 1.3 *- continued*

TYR	TIBER	Italy	41.90	12.48	16.6	*84.211*	7.38	446	*84.211*
TYR	VOLTURNO	Italy	41.02	13.92	5.5	*95.013*	3.10	564	*95.013*
TYR	MEDJERDA	Tunisia	37.18	10.17	21.8	*76.126*	0.95	44	*76.126*
TYR	OMBRONE	Italy	42.65	11.00	2.6	*95.013*	0.79	304	*95.013*
TYR	TAVIGNANO	France	42.08	9.50			0.06		*97.005*
ADR	DRINI	Albania	41.75	19.57	14.2	*96.027*	11.39	804	*96.027*
ADR	BUNA	Albania	41.85	19.28	5.2	*96.027*	10.09	1944	*96.027*
ADR	VIJOSE	Albania	40.38	19.80	6.7	*96.027*	6.15	917	*96.027*
ADR	MATI	Albania	41.65	19.53	2.4	*96.027*	3.25	1332	*96.027*
ADR	SEMANI	Albania	40.73	19.55	5.7	*96.027*	3.02	535	*96.027*
ADR	SHKUMBINI	Albania	41.07	19.73	2.5	*96.027*	1.94	792	*96.027*
ADR	ISHMI	Albania	41.67	19.56	0.7	*96.027*	0.66	985	*96.027*
ADR	ERZENI	Albania	41.40	19.38	0.8	*96.027*	0.51	671	*96.027*
ADR	NERETVA	Croatia	43.03	17.65	11.8	*99.001*	13.80	1169	*99.001*
ADR	KRKA	Croatia	43.72	15.97	2.0	*99.001*	2.01	1015	*99.001*
ADR	ZRMANJA	Croatia	44.08	15.63	0.9	*99.001*	1.39	1533	*99.001*
ADR	CETINA	Croatia	43.35	16.70	1.5	*99.001*	1.31	895	*99.001*
ADR	MIRNA	Croatia	45.33	13.55	0.5	*99.001*	0.29	633	*99.001*
ADR	PO	Italy	44.88	11.65	70.0	*84.211*	47.80	683	*01.001*
ADR	ADIGE	Italy	45.10	11.83	12.0	*84.211*	7.29	610	*84.211*
ADR	BRENTA	Italy	45.18	12.30	1.6	*74.036*	2.32	1487	*74.036*
ADR	PESCARA	Italy	42.47	14.22	3.1	*95.013*	1.70	548	*95.013*
ADR	RENO	Italy	44.62	12.27	3.4	*74.036*	1.40	412	*74.036*
ADR	BIFERNO	Italy	41.92	15.03	1.3	*74.036*	0.67	516	*74.036*
ADR	METAURO	Italy	43.83	13.05	1.4	*74.036*	0.43	307	*74.036*
ADR	FORTORE	Italy	41.63	15.08	1.1	*74.036*	0.43	381	*74.036*
ADR	OFANTO	Italy	41.37	16.22	2.7	*74.036*	0.37	136	*95.013*
ION	AKHELOOS	Greece	38.60	21.23	5.5	*97.014*	5.67	1023	*97.014*
ION	CRATI	Italy	39.72	16.52	1.3	*74.036*	0.86	647	*74.036*
ION	SINNI	Italy	40.14	16.71	1.1	*74.036*	0.71	623	*74.036*
ION	SIMETO	Italy	37.40	15.10	1.8	*74.036*	0.54	295	*74.036*
ION	BRADANO	Italy	40.38	16.85	2.7	*74.036*	0.21	77	*74.036*
AEG	AXIOS	Greece	40.63	22.97	24.7	*84.211*	4.90	198	*97.014*
AEG	STRYMON	Greece	40.80	23.87	16.5	*94.064*	2.59	157	*94.064*
AEG	ALIAKMON	Greece	40.52	22.53	9.5	*84.211*	1.17	123	*97.007*
AEG	NESTOS	Greece	40.68	24.73	5.7	*94.064*	1.03	179	*94.064*
AEG	PINIOS	Greece	39.90	22.75	9.8	*97.017*	0.67	69	*97.015*
AEG	EVROS	Greece/Turkey	40.88	26.17	55.0	*97.014*	6.80	124	*97.014*
AEG	BUYUK MENDERES	Turkey	37.67	27.33	19.6	*89.175*	4.70	240	*89.175*
AEG	GEDIZ	Turkey	38.58	26.80	15.6	*83.244*	1.87	120	*83.244*
NLE	SEYHAN	Turkey	36.72	34.88	20.0	*94.066*	7.20	360	*94.066*
NLE	CEYHAN	Turkey	37.03	35.82	20.5	*83.244*	7.10	346	*94.066*
NLE	MANAVGAT	Turkey	36.78	31.43	1.3	*83.244*	4.99	3780	*96.029*
NLE	NAHRELASI	Turkey	36.12	35.92	22.6	*83.244*	2.70	119	*83.244*
NLE	GOKSU	Turkey	36.32	34.03	10.1	*92.009*	2.50	248	*92.009*
NLE	LAMAS	Turkey	36.62	34.30			2.20		*96.029*
SLE	NILE	Egypt	31.43	31.80	2870.0	*78.090*	6.00	2	*93.027*
SLE	KISHON	Israel	32.82	35.03	1.1		0.06	58	*97.015*

For source indexes, see reference list

We retained for our study data on 74 rivers. They are listed in table 1.3 according to the major sub-basins to which they are discharging. When ranking according to total annual water discharge, the ten largest rivers are the Rhone, Po, Drini, Neretva, Buna, Ebro, Tiber, Adige Seyhan and Ceyhan rivers. Together they bring about 170 km^3/yr of water to the Mediterranean Sea, which is about half of the overall freshwater input by rivers (see chapter II). The Rhone and the Po rivers alone still account for one third of this value. The Rhone is nowadays the largest freshwater source since the closure of the Aswan dam in the sixties of the last century. Before this, the Nile held this position, with an average discharge of about 84 km^3/yr (Kempe, 1993). In bringing the water from his headwaters in the Southern Hemisphere to the north over a distance of about 6500 km, the Nile River played a very particular role in the hydrology of the Mediterranean.

When ranking according to basin size, the ten largest rivers are the Nile, Rhone, Ebro, Po, Evros, Moulouya, Cheliff, Isser, Axios and Nahrelasi rivers. Many more southern rivers are represented in this list, underlining the strong climatic contrast between the north and the south.

The drainage intensities (water discharge divided by basin area) in the different rivers largely reflect the climatic particularities in the Mediterranean region (see above). Although the differences between individual rivers of the same sub-basin is sometimes important, it can be generalised that the lowest drainage intensities are typical for the rivers of the S-Levantine and Central basins. In the order of increasing values follow then the rivers of the Alboran Sea, the ones of the S-Western, Aegean, Tyrrhenian, N-Levantine, N-Western, and Ionian basins, and finally the rivers of the Adriatic Sea. Of the latter basin, numerous rivers have values even above 1000 and 1500 mm, such as the Buna and Mati rivers in Albania, and the Zmanja and Neretva rivers in Croatia. These values are high compared to other world rivers, underling the fact that there is important water excess in this region (see also fig. 1.2d). Note that the Amazon River has an average drainage intensity of only about 1100 mm. Nevertheless, one has also to mention here that in some cases these values may be misleading. Especially in Croatia, river basins can be connected to each other via karst networks, and water may be imported from outside the catchments.

1.4.2 - Hydrological regimes

Due to the strong seasonal contrast of climate, the hydrological regime of the Mediterranean rivers is quite particular compared to other regions. The differences between low and high water discharge can be extreme. Often, most of the water discharge occurs during short floods. In the large and medium-sized river basins situated in north and central Europe, wide-ranging and continuous precipitation is commonly the main factor in flood generation, often also in association with snowmelt. Intense rainfall falling on small catchments is the main cause of floods in the Mediterranean area. In some areas along the Mediterranean cost, the recorded maximum daily rainfall is close to the mean annual rainfall (Estrela et al., 2001).

As a consequence, the ratio of peak discharge on mean annual discharge in drainage basins of 1000 to 10 000 km^2, which is quite typical for Mediterranean rivers, is frequently about one order of magnitude greater than for rivers in Non-Mediterranean areas (fig. 1.5). This also represents a major difficulty for the monitoring of these rivers. Gauging stations have to be calibrated for extreme water levels and the equipment has to be designed to resist to violent flash floods. Monitoring of water quality parameters, as far as they should be used for the calculation of fluxes, is even more difficult to realise because almost all of the transfer occurs during these floods (especially in the particulate phase). Flash floods often escape to regular sampling campaigns.

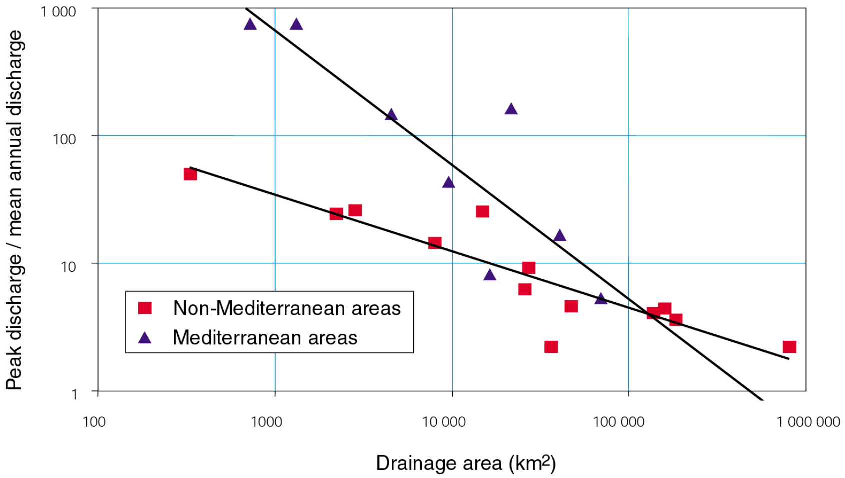

Fig. 1.5 - Ratio between peak discharge and mean annual discharge of Mediterranean rivers in comparison with other Non-Mediterranean rivers (Estrela et al., 2001).

With respect to seasonal variation of the water discharge, one can notice that by far most of the Mediterranean rivers have lowest values during summer (July to September) because of the strongly reduced precipitation and the elevated temperatures during this season. Figure 1.6 shows the 1969-79 average monthly hydrographs for some of the major Mediterranean rivers. Maximum values are normally observed between February and May. The February maximum is typical for the rivers that are rainfall dominated (such as the Tiber and Arno rivers), since rainfall is strongest in winter (see above). When the headwaters reach up to highly elevated areas, which is often the case, snowmelt discharge becomes dominant. This is shifting the maximum discharge to April or May (e.g. the Drini or Ceyhan rivers). Often, both regimes are superimposed. An exception to the general trend is the Adige River in the northeast of Italy, where maximum discharge occurs in early summer. Winter discharge is quite low. In this part of the Mediterranean drainage basin, climate is rather continental (fig. 1.3a-d). Certain tributaries of the Po are under a similar climate, which obviously has an impact on the hydrograph of this river too. Finally, it may be pointed out that the accentuation of the seasonal contrast towards the south and the east has naturally also a strong impact on the rivers in these areas. Almost all of the discharge occurs during the first half of the year, whereas the second half is very dry (e.g. Moulouya and Ceyhan rivers).

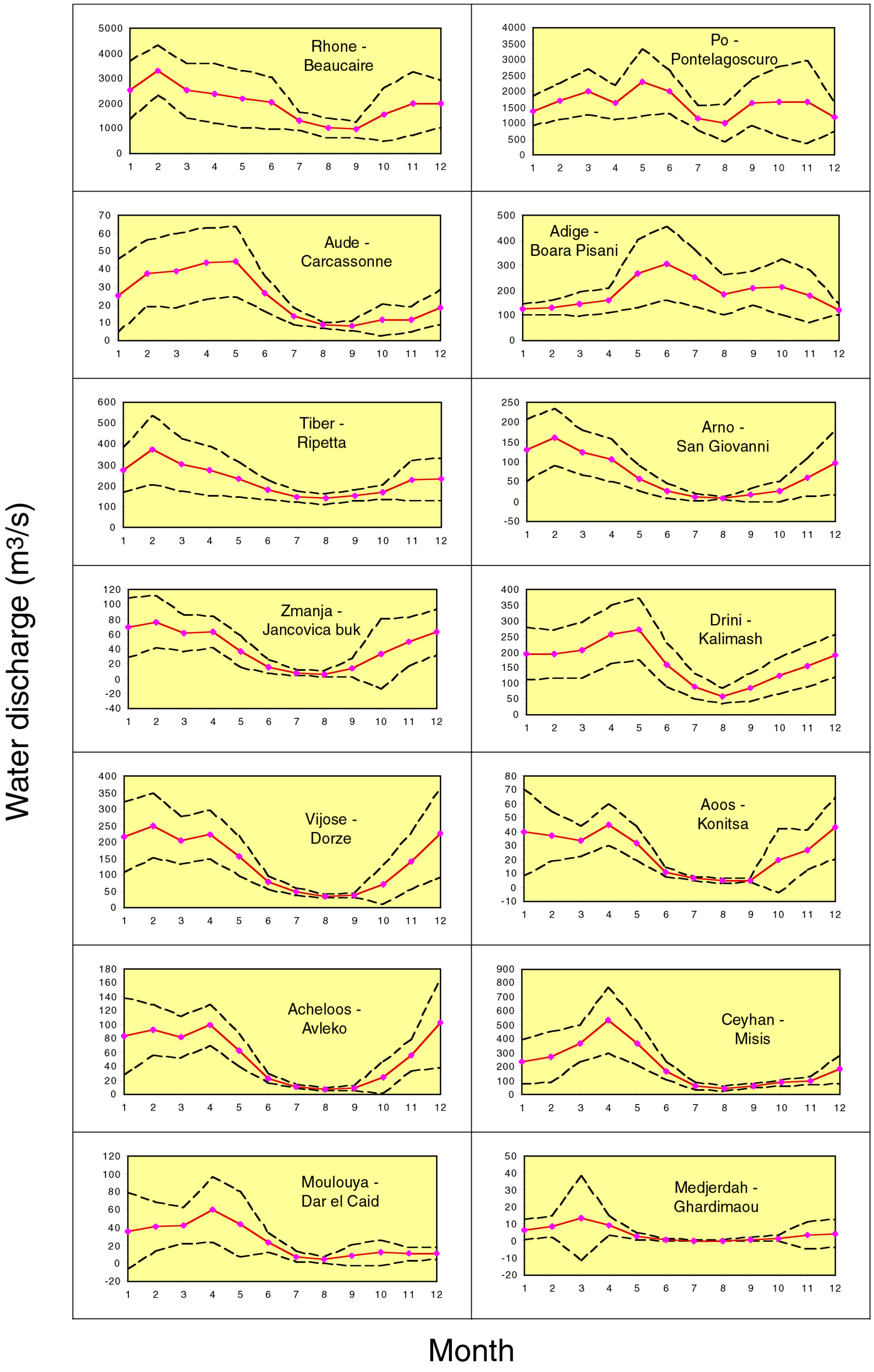

Fig. 1.6 - Seasonal variation of discharge in some Mediterranean rivers. Solid line: 1969-79 average; dashed lines: standard deviation. Data sources: Medhycos (2001) and/ or Vörösmarty et al. (1998). For more details, see chapter II

1.4.3 - River damming

The artificial damming of rivers for the purpose of water use is not a recent phenomenon. The earliest large dams are located in Spain and are believed to date from the 2nd century AD (Leonard and Crouzet, 1999). Nevertheless, it was mainly during the second half of the last century that the overall rate of dam construction in Europe was highest (fig. 1.7). This concerned many rivers flowing to the Mediterranean. Spain is currently the country having the greatest number of large reservoirs (height of the dam wall ≥15m), with 849 dams in 1997. For the same year, 521 dams were registered in France and 425 in Italy (Leonard and Crouzet, 1999). In Greece, this was only 13, but these dams were larger on average than the above mentioned ones. No precise figures were available to this report for the other countries bordering to the Mediterranean.

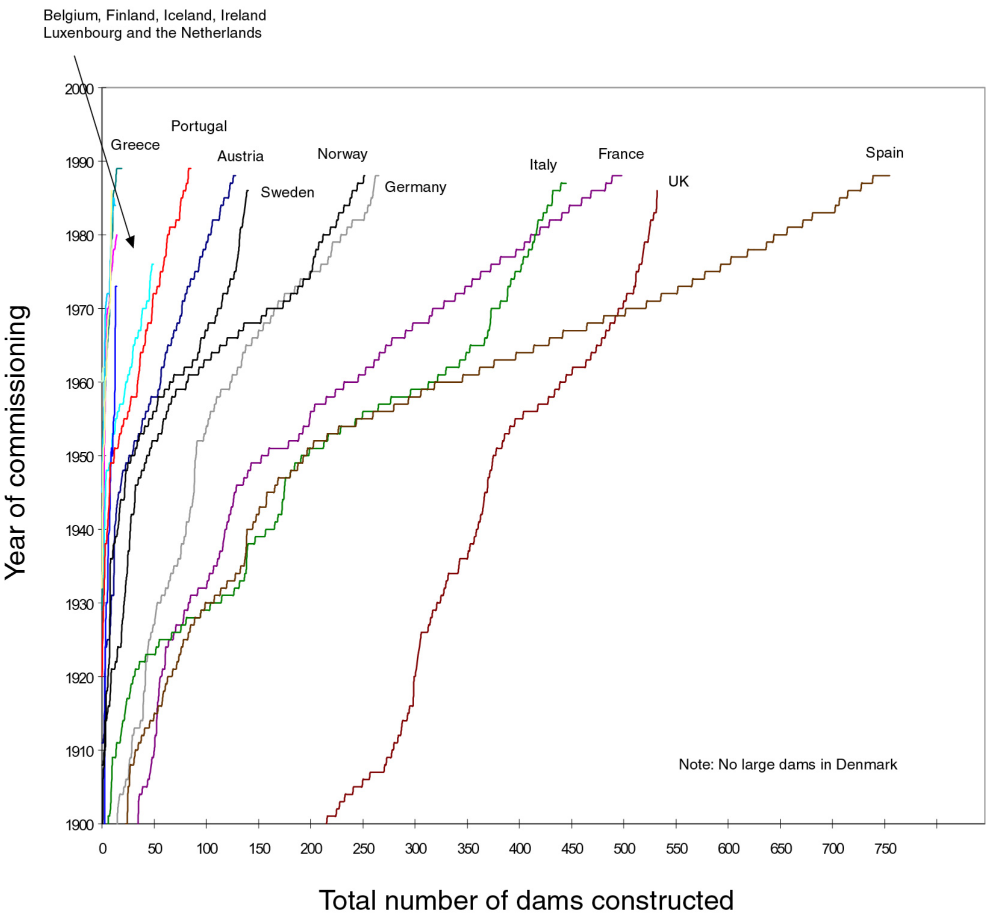

Fig. 1.7 *- Evolution of reservoir construction in some European countries (Leonard and Crouzet, 1999).*

The principal reasons for dam construction are hydroelectric power generation, irrigation, public water supply, and flood control. Low flow enhancement, recreation, fish farming, transport and navigation facilitation, and spoil storage are additional purposes. Considering the presence of large reservoirs in river basins is important for the understanding of water quality and matter transfer in these rivers because their impact on the natural functioning can be considerable. In the Mediterranean area, where water shortage is endemic and water extraction for irrigation and public water supply are the major reasons for the reservoir constructions, this impact is already highly visible with respect to water discharge. Especially in the hot and dry climates of the south, the reduction of natural water discharge due to river damming can be dramatic. A well-known case where the ongoing construction of dams during the 20th century was accompanied by a continuous reduction in mean annual discharge is the Ebro River in Spain. Today, a total of 128 reservoirs exist in the Ebro basin, with a storage capacity of about 6.51 km^3. Concomitant reduction in water discharge was estimated to be about 29% (Ibanez et al., 1996). Also the seasonality of the river's hydrograph was strongly smoothed.

Further south, the examples of water discharge reduction due to damming are even more extreme. Snoussi et al (2002) estimated that the discharge of the Moulouya River dropped by about 47% after the construction of the Mohamed V dam in Morocco. Zahar and Albergel (1999) reported that the closure of the Sidi Salem Dam in Tunisia led to a reduction of the mean annual discharge of the Medjerdah River by 65% due to diversion for irrigation and evaporative losses. But the most famous example is naturally the Nile River. After the closure of the Aswan Dam in Egypt, probably less than 5% of the 84 km^3 of water that enters on average the reservoir ends up in the Mediterranean (Kempe, 1993). The average residence time of the water is about 2 years and direct evaporation from the reservoir alone is in the range of 10 km^3/yr. The bulk of the river water ends up on the fields further downstream via irrigation.

Chapter II - Water discharge

2.1 - Introduction

Water discharge is the most important factor controlling the matter transfer from land to the sea by rivers. Even if the average concentrations of different pollutants can be determined with reasonably good precision, flux estimates can only be as good as the estimates for the corresponding water discharge. Moreover, for many dissolved and particulate species in rivers, concentrations are not independent from runoff, and an evaluation of possible trends has to take into account the hydrological conditions during which the observations have been made.

For these reasons, we intend in this chapter to determine reliable values for the overall freshwater inputs to the Mediterranean Sea by rivers. These values can then be used in the following chapters as a basis for calculating fluxes. Water fluxes can evolve during time because of climate change and anthropogenic water use in the basins, and these figures cannot be given without mentioning the corresponding reference period. A detailed evaluation requires the availability of a huge amount of hydrological records for the rivers draining to the Mediterranean Sea. The acquisition of these data, even if they might exist, is naturally beyond the scope of this study. Nevertheless, we consider that the hydrological and climatic information that can be found in scientific publications or that is nowadays distributed via the internet is sufficient to detect general trends which can then be extrapolated to the entire Mediterranean, to its sub-basins and/or to terrestrial catchments at regional scales. This is the approach we follow in this chapter. It means that the given values represent general evolutions that may be representative for time slices of about 5 to 10 years but they cannot be attributed to individual calendar years.

Three major reference periods are distinguished: the beginning of the 20th century (1900-1920), the period around 1960 to 1970, and the end of the 20th century (1995-2000). The latter corresponds more or less to the actual situation. Looking at the evolution since the beginning of the 20th century is interesting because it allows an estimate for the amplitude of the long-term variability of river discharge, which can be important for the general understanding of possible changes that might have been occurred in the marine ecosystem. The distinction between the periods before and after the sixties is somewhat arbitrary. For many rivers, data are only available for the second half of the 20th century, especially after 1960. Trend estimates can hence be more precise for the second part of the last century than for the first one. The 1960 to 1970 limit, however, may also correspond to some physical change in many river systems. The construction of numerous dams falls in this period (see chapter 1) and for certain regions, such as Spain, climate changed markedly since this time (see below). The other reason we selected this limit is the fact that for flux calculations, data on water quality in rivers are rarely available before 1970.

2.2 – Climate change and evolution of rainfall

Climate change, and especially changes in precipitation over time, has to be considered first when looking at the evolution of freshwater discharges to the sea by rivers. In many cases, time series for precipitation are more easily available than discharge records, and can therefore be used as extrapolation matrix for discharge at temporal and spatial scales. On the other hand, any evolution in river discharge should be interpreted in conjunction with the evolution of precipitation over the corresponding drainage basin. Anthropogenic activities, such as river damming and/or increased water extraction for irrigation can, therefore, be detected from these comparisons between water discharge and precipitation.

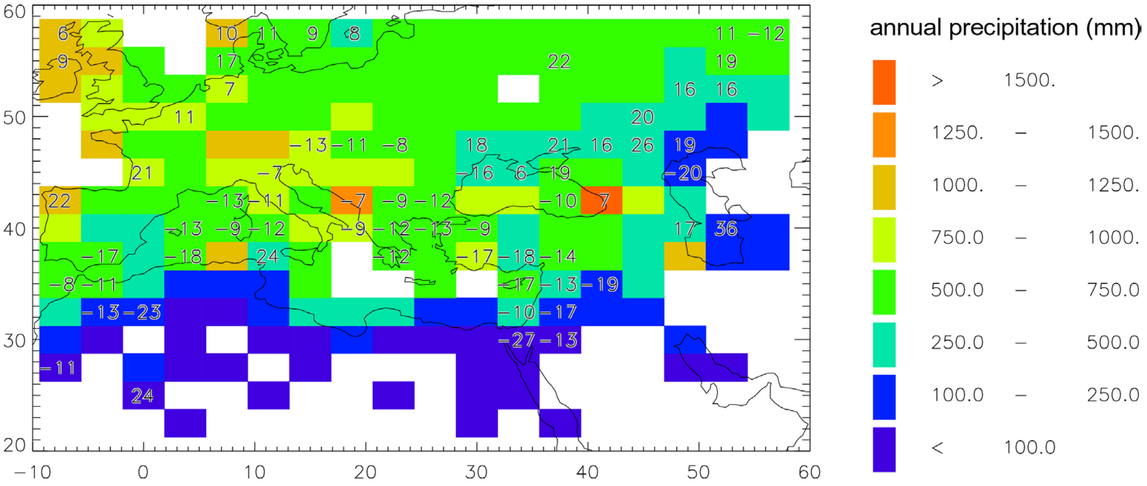

Fig. 2.1a *- Mean annual rainfall during 1900 to 1998 over the Mediterranean region according to Hulme (1999). The numerical values in the grids indicate the rainfall changes in percent when the evolution follows a significant trend (P < 0.1). For further information, see text.*

In our study, we consulted the data set of Hulme (1999) for the evaluation of rainfall trends over the Mediterranean drainage basin. These data represent a global reconstruction of monthly precipitation from 1900 to 1998 in a spatial grid point resolution of 2.5° latitude by 3.75° longitude. Although this resolution is coarse, it should be sufficient to detect general trends that might have affected river discharge in the Mediterranean region. The maps in figures 2.1a (1900-1998 evolution) and 2.1b (1960-1998 evolution) show the grid points included in the data set, as well as the range of average annual precipitation attributed to these grids. A comparison with figure 1.2b (chapter I) allows estimating the degree of simplification of the real precipitation patterns related to the coarse resolution. For some of the grids in the dry parts of Africa, the records can be incomplete, whereas for the rest of the grids, only very few missing values are encountered in the database.

We performed trend analyses for all of the grids on the basis of the Mann-Kendall test in order to detect possible changes (Mann, 1945; Kendall, 1975). As far as a significant trend was detected (in general, $P \leq 0.05$), we determined the long-term change in precipitation by linear regression between the five-year running mean of mean annual precipitation and time. In the figures 2.1a and b, this is expressed by numerical values within the grids. These values indicate the difference between the regression model values for the beginning and for the end of the record, in percent of the first value. Negative values indicate therefore a precipitation decrease. In addition, we also determined the general evolution of the average values for larger units such as the entire western or eastern basin, or for large river basins. These data are represented in table 2.1 and in figure 2.2.

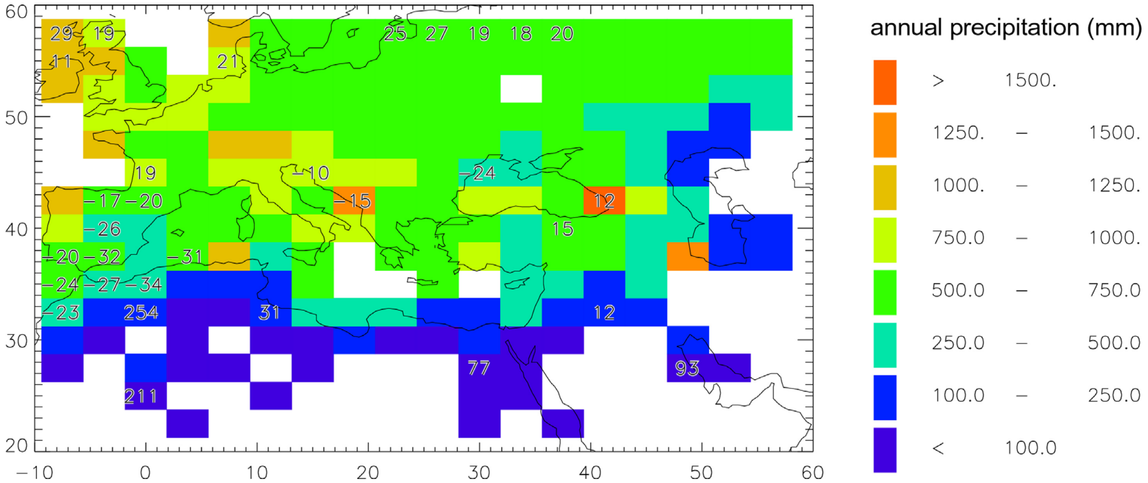

Fig. 2.1b *- Mean annual rainfall during 1960 to 1998 over the Mediterranean region according to Hulme (1999). The numerical values in the grids indicate the rainfall changes in percent when the evolution follows a significant trend (P < 0.1). For further information, see text.*

It is a striking feature that for many grids over the Mediterranean drainage basin, the evolution during the last century is characterised by negative rainfall trends (fig. 2.1a). Positive trends can be found further North, but they are almost absent in the Mediterranean region. The average precipitation decrease is about 6% for the western basin, and about 10% for the eastern basin (not including the Nile).

When only looking at the evolution from 1960 to 1998 (fig. 2.1b), less grid elements depict significant trends. Especially in Spain, and over the terrains draining to the Alboran Sea, a severe precipitation decrease is found. The other region where average precipitation decreased is the Adriatic coast of Albania and Croatia. Because average precipitation is very high in this region, this decrease affected significantly the overall precipitation input to the entire Adriatic Sea (table 2.1).

One can also notice that the evolution of rainfall in the Po and the Rhone rivers, the two largest north-Mediterranean rivers draining the Alps, is characterised by marked fluctuations following more or less a 20 to 25 year cycle (fig. 2.2). A general trend, however, is absent. Further south, overall precipitation decrease and the fluctuations become smoothed. In the Nile River, rainfall decreased markedly since about 1960, leading to an overall reduction of rainfall of almost 12% for the entire basin. This is important because this effect is superimposed to the reduction of the Nile discharge related to the closure of the Aswan Dam in 1964, enhancing thus the water discharge deficit of this river.

Table 2.1 *- Precipitation (P) changes in some large catchments of the Mediterranean region.*

Basin	reference period	average P (mm)	P change (%)
Rhone	1900-98	843	-- *
	1960-98	846	--
Tiber	1900-98	745	-10.3
	1960-98	733	--
Po	1900-98	898	--
	1960-98	894	--
Danube	1900-98	748	--
	1960-98	741	--
Nile	1900-96	902	-4.8
	1960-96	886	-11.6
Western Basin	1900-98	624	-6.0
	1960-98	611	--
Eastern Basin (without Nile)	1900-96	510	-9.7
	1960-96	497	--
Adriatic Basin	1900-98	834	-6.8
	1960-98	824	-9.5

* No value means that trends were not significant at $P \leq 0.05$

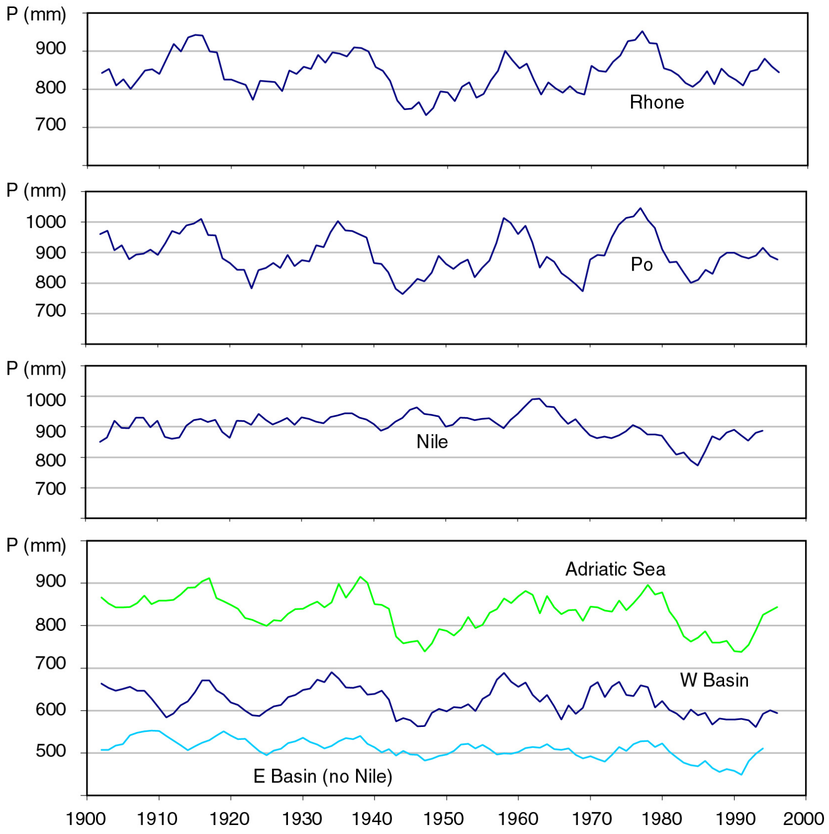

Fig. 2.2 *- 1900 to 1998 evolution of rainfall in some of the large catchments of the Mediterranean region. The lines represent the 5-year running mean of mean annual precipitation.*

2.3 – Water discharge trends in Mediterranean rivers

We included discharge records of about 30 rivers in our evaluation of the evolution of water discharge over time in the Mediterranean region. They are represented in figures 2.3a and b. Most of the data were downloaded from the Med-Hycos database, a special site on the hydrology of the Mediterranean Sea (Medhycos, 2001). They are currently updated and include also most recent years. Other time series of river discharge were obtained from the Global River Discharge Database RivDIS (Vörösmarty et al., 1998). These data were originally published by UNESCO and normally stop in the 80's of the last century. In General, time series less than 20 years were not taken into account in our analyses. The spatial distribution of the rivers covers most of the Mediterranean 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. Especially Turkish rivers are underrepresented in our data.

Trend analyses were performed on the basis on the Mann-Kendall test in a similar way than for the time series of precipitation (see above). The time series of the river data do not necessarily cover the same periods and the comparison of trends between rivers has, therefore, to be done with caution. Moreover, in some cases, the time series are not complete and certain years are missing, which can affect the significance of the detected trends. Another problem is that the gauging stations are not always situated close to the river mouth and only reflect a certain portion of the overall discharge. Also the comparison of river basins of different sizes has to be done with caution, since small basins may be much more subjected to local patterns. Despite these limitations, we consider that the overall data still allow a good overview of the general evolution of Mediterranean river discharges. The succession of dry and wet periods is normally well correlated for rivers of the same regions, indicating that records are representative for these regions.

2.3.1 – Long-term trends

Long-term trends were established for the rivers for which records of about 50 years or more were available (fig. 2.3a), and the results are given in table 2.2. This concerns mainly the northwestern European rivers such as the Rhone River, and Italian rivers, the country for which the data coverage is the best. In most of the cases, clear negative trends are prominent. The only case where a positive trend was detected is the Tet River, a small coastal river in the southwest corner of the Mediterranean coast of France. This increase is in agreement with the evolution of rainfall in this part of the Pyrenees (Moisselin, 2002). The Po and the Rhone rivers do not depict any long-term trend and the records are in good agreement with the evolution of rainfall (fig. 2.2 and 2.3a). Also the discharge of the Danube River does not show any trend (although the Danube does not discharge into the Mediterranean Sea, we included it here for comparison), indicating that this may be a general feature for the rivers taking their headwaters in the Alps.

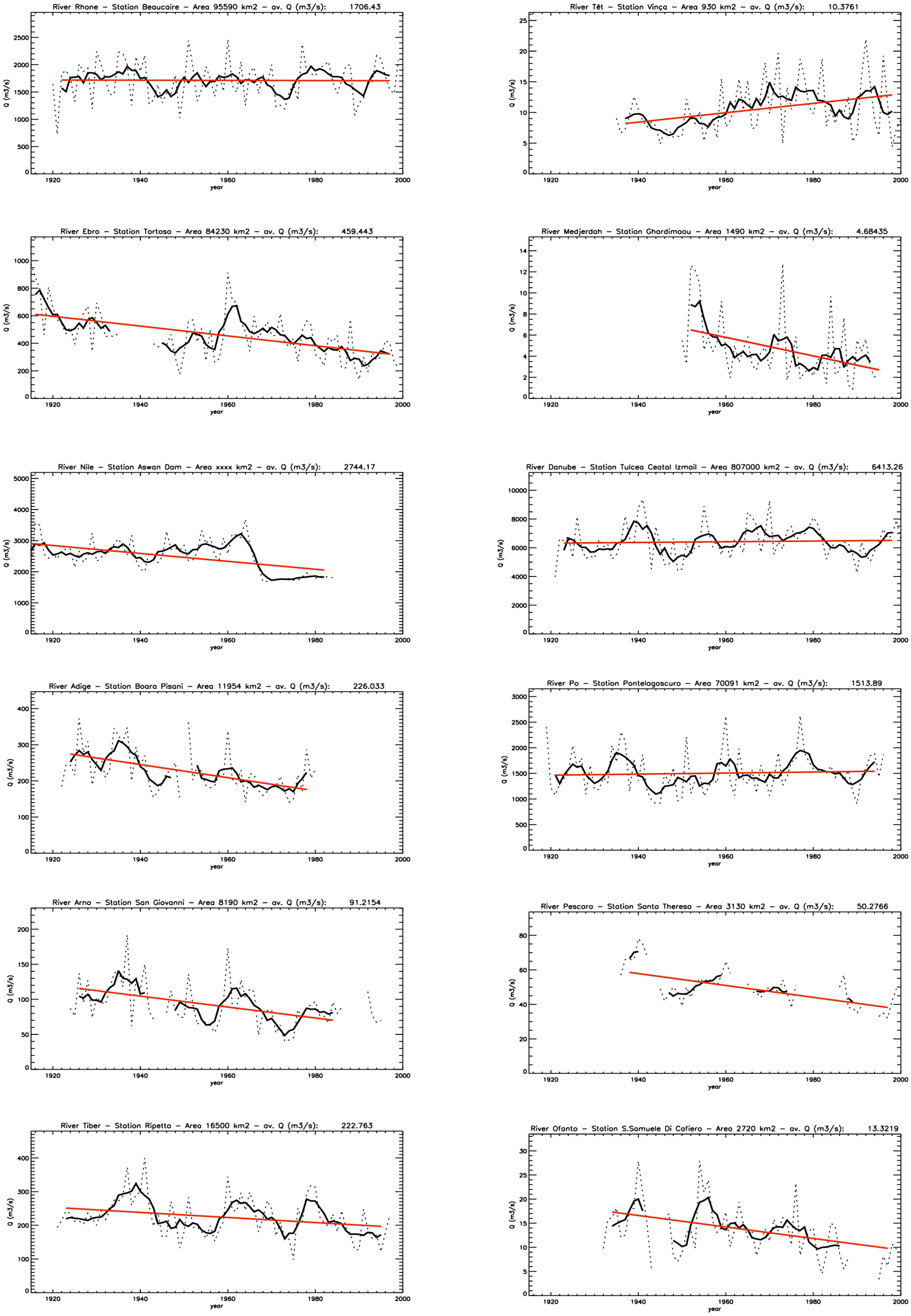

Fig. 2.3a *- Long-term variations of discharge in some Mediterranean rivers since about 1920 (dashed line: individual years, solid line 5 year running mean). Trends (red line) are calculated automatically; they are only significant when this is indicated in table 2.2*

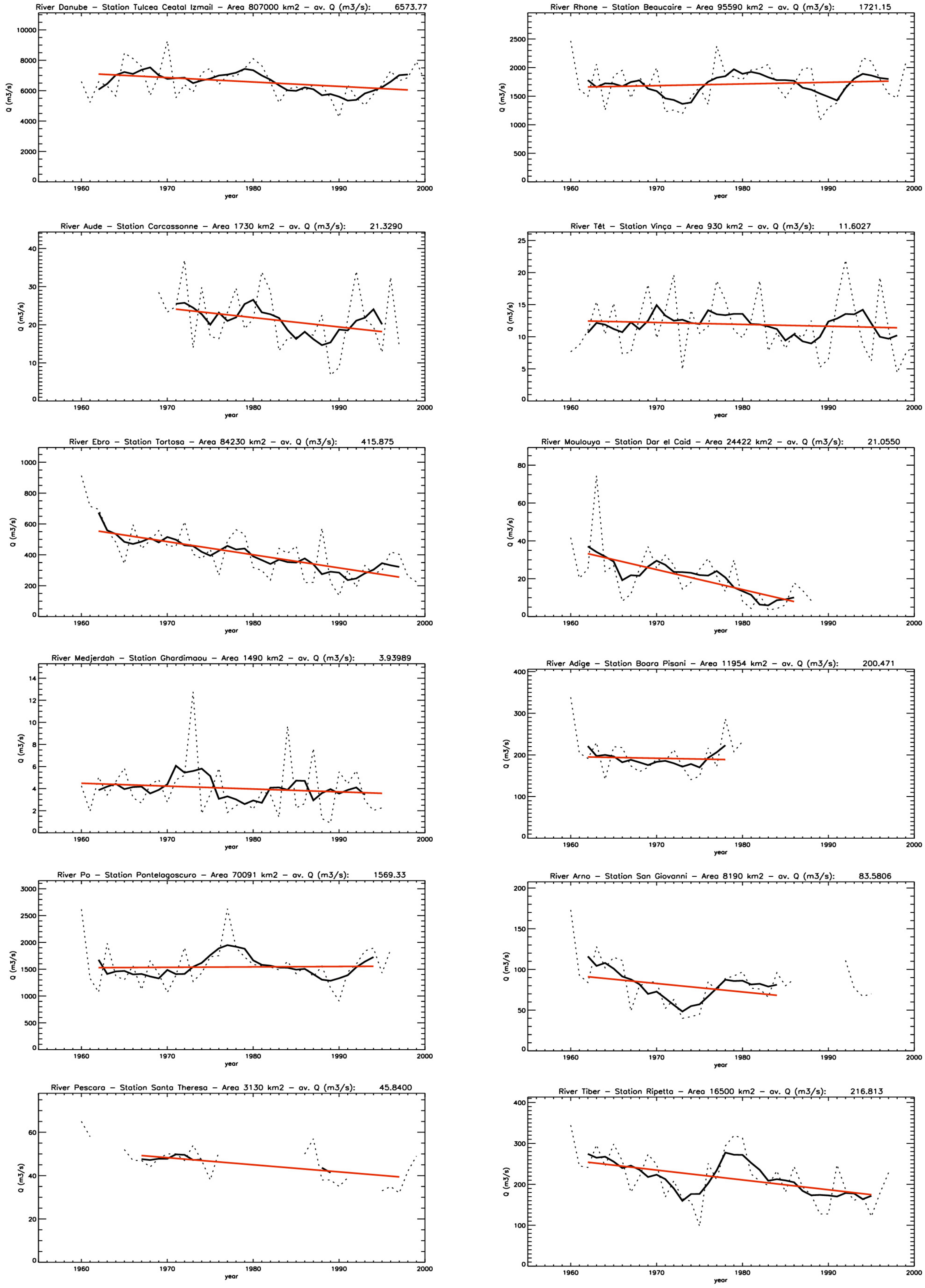

Fig. 2.3b - Variations of discharge in some Mediterranean rivers since 1960 (dashed line: individual years, solid line 5 year running mean). Trends (red line) are calculated automatically; they are only significant when this is indicated in table 2.3

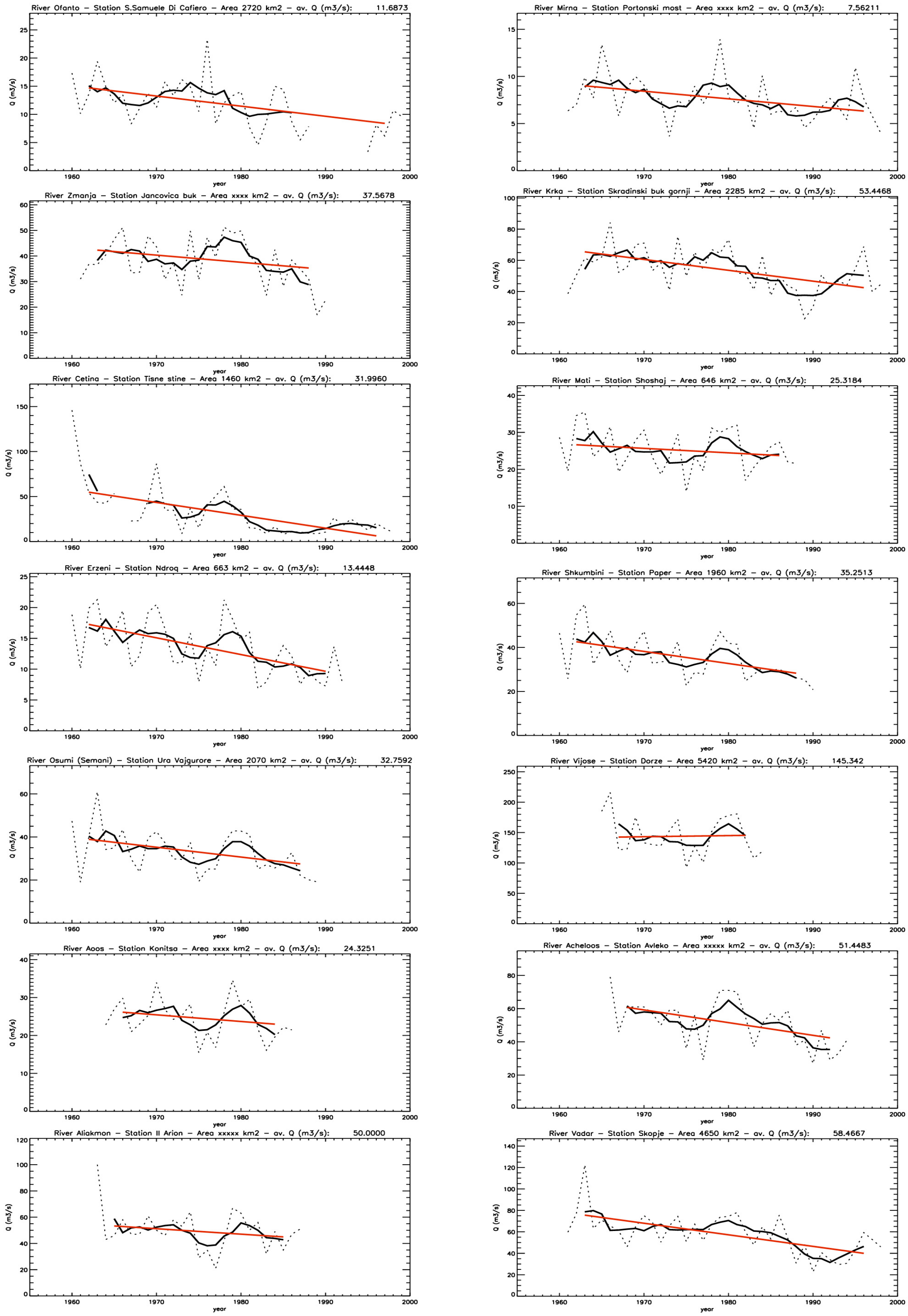

Fig. 2.3b *- continued*

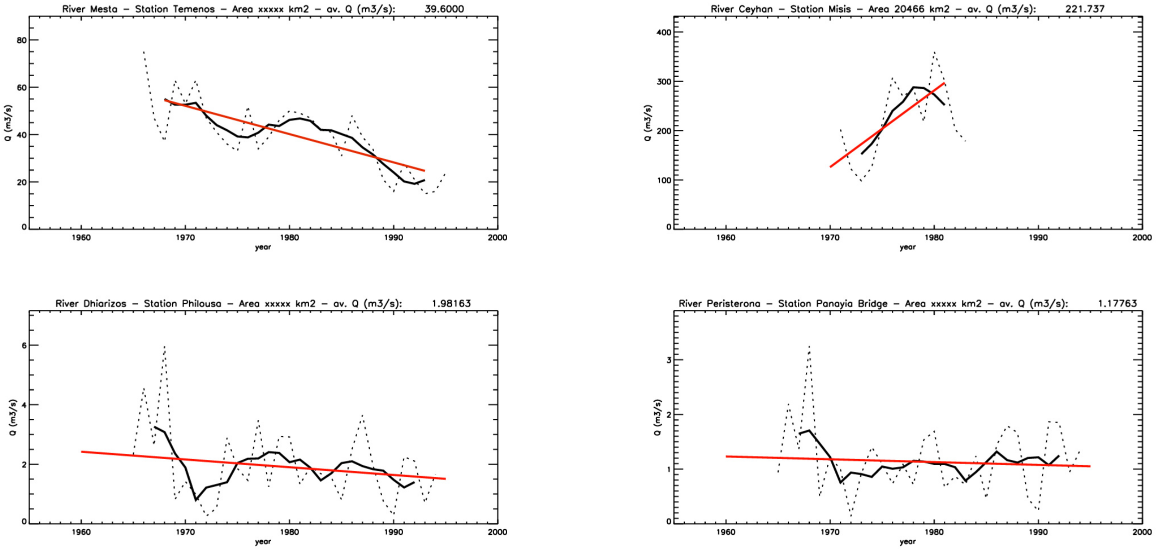

Fig. 2.3b - *continued*

Tab. 2.2 - *Long-term trends of water discharge in some Mediterranean rivers.*

Code basin[1]	River	Country	Station	Area (km^2)	Record period start	Record period end	Average Q (m^3/s)	Ref.	Q change (%)
NWE	Rhone	France	Beaucaire	95590	1920	1999	1706	(3)	--(2)
NWE	Têt	France	Vinça	930	1935	2000	10	(4)	56.8
NWE	Ebro	Spain	Tortosa	84230	1914	1999	459	(3)	-47.3
Black Sea	Danube	Rumania	Tulcea Ceatal Izmail	807000	1921	2000	6413	(3)	--
ADR	Adige	Italy	Boara Pisani	11954	1922	1980	226	(5)	-35.8
ADR	Po	Italy	Pontelagoscuro	70091	1919	1996	1514	(3)	--
NWE	Arno	Italy	San Giovanni	8190	1924	1995	91	(3)	-39.2
ADR	Pescara	Italy	Santa Theresa	3130	1939	1999	50	(3)	-34.7
TYR	Tiber	Italy	Ripetta	16500	1921	1997	223	(3)	-21.6
ADR	Ofanto	Italy	S. Samuele di Cafiero	2720	1930	1999	13	(3)	-43.4
TYR	Medjerdah	Tunisia	Ghardimaou	1490	1950	1995	5	(5)	-55.6
SLE	Nile	Egypt	Aswan Dam		1871	1984	2744	(5)	-40.3

(1) see Table 1.1 (chapter I)
(2) no value means that trends were not significant at $P \leq 0.05$
(3) Medhycos (2001)
(4) Stucky (2001)
(5) Vörösmarty et al. (1998)

Except the Po River, all Italian rivers show clear negative trends. This may be the combined action of climate change and increased anthropogenic water use in the basins. It is remarkable that the water discharge reduction is less important for the Tiber River (about –20%) than for the other Italian rivers (in the range of –35 to –45%). The record for the Tiber is more complete than for the other rivers, making a direct comparison somewhat difficult. But it is possible that these differences mainly reflect the evolution of rainfall over Italy. When looking at the precipitation map in figure 2.1a, one can see that a reduction of rainfall occurred in the north (Arno, Adige) and in the south (Ofanto), but not in the centre of the country.

2.3.2 – Recent trends since 1960

Data coverage since 1960 is much better than from the beginning of the 20th century, and more rivers could be included in the trend analysis (tab. 2.3). Because of the shorter time span considered, it is possible that general trends may be overwhelmed by the general cyclicity of dry and wet periods, which seem to occur, at least in the northern part of the Mediterranean region, in time intervals of about 20-25 years (see above). Probably also as a consequence of this, only for about half of the rivers, significant trends were found. But in all cases, these trends are negative.

The strongest reduction is found for rivers that were affected both by the construction of dams and by precipitation decrease, such as the Ebro River in Spain and/ or the Moulouya River in Morocco. The strongest reduction is found for the Cetina River in Croatia where large artificial reservoirs (Peruca and Busko Blato) have been built for hydropower plant, water supply and protection against flood. In general, discharge reduction is frequent in the rivers of the Eastern Mediterranean, mainly when the records extend to the recent years and do not stop in the eightieth. It seems also that the reduction becomes more important from the north to the south. Many Greek rivers suffered from a reduction of up to half of their original discharge (Skoulidikis and Gritzalis, 1998). When going further east, data coverage is not sufficient, especially for Turkish rivers. We only found a short record for the Ceyhan River, and data for two very small rivers on Cyprus. The latter show no clear evolution, but they may not really be representative for the entire region. Nevertheless, precipitation rather increased in this part of the Mediterranean (contrary to Greece), and also the headwaters of the Euphrates River depicts no clear trend in discharge (not shown here). We concluded therefore that there might have occurred a small reduction in discharge due to water use in the Turkish part of the eastern drainage basin, but certainly less important than in Greece.

Finally, it is worth being mentioned that also for the evolution since 1960, the Po and the Rhone rivers do not follow the general trend of a reduction in water discharge. This is important because also in these basins, impoundments and dams are frequent. In the Rhone, for example, a considerable part of the tributary discharge from the Durance River has been deviated to the lake of Berre (near Marseille) during the sixties, leading to an overall reduction of the Rhone discharge of about 100 m^3/s on average (Vivian, 1989). In the discharge record of the Rhone (fig. 2.3a,b), this is not visible. Apparently, human activities have less impact on the amount of annual water flow out of these basins. Or this impact is compensated by more humid conditions. Note that when looking at the evolution of precipitation in the Rhone basin (fig. 2.2), it seems that the values tend to increase since the middle of the last century.

__Tab. 2.3__ - Discharge trends since 1960 in some Mediterranean rivers.

Code basin(1)	River	Country	Station	Area (km^2)	Record period		Average Q		Q change
					start	end	(m^3/s)	Ref.	(%)
Black Sea	Danube	Rumania	Tulcea Ceatal Izmail	807000	1960	2000	6574	(3)	--(2)
NWE	Rhône	France	Beaucaire	95590	1960	1999	1721	(3)	--
NWE	Aude	France	Carcassonne	1730	1969	1999	21	(3)	--
NWE	Têt	France	Vinça	930	1960	2000	12	(4)	--
NWE	Ebro	Spain	Tortosa	84230	1960	1999	416	(3)	-53.8
ALB	Moulouya	Morocco	Dar el Caid	24422	1960	1988	21	(5)	-76.1
TYR	Medjerdah	Tunisia	Ghardimaou	1490	1960	1995	4	(5)	--
ADR	Adige	Italy	Boara Pisani	11954	1960	1980	200	(3)	--
ADR	Po	Italy	Pontelagoscuro	70091	1960	1996	1569	(3)	--
NWE	Arno	Italy	San Giovanni	8190	1960	1995	84	(3)	--
ADR	Pescara	Italy	Santa Theresa	3130	1960	1999	46	(3)	-20.0
TYR	Tiber	Italy	Ripetta	16500	1960	1997	217	(3)	-31.2
ADR	Ofanto	Italy	S.Samuele Di Cafiero	2720	1960	1999	12	(3)	-42.8
ADR	Mirna	Croatia	Portonski most		1961	1998	8	(3)	-29.7
ADR	Zmanja	Croatia	Jancovica buk	907	1961	1990	38	(3)	--
ADR	Krka	Croatia	Skradinski buk gornji	2285	1960	1998	53	(3)	-35.1
ADR	Cetina	Croatia	Tisne stine	1460	1960	1998	32	(3)	-88.5
ADR	Mati	Albania	Shoshaj	646	1960	1988	25	(3)	--
ADR	Erzeni	Albania	Ndroq	663	1960	1992	13	(3)	-44.1
ADR	Shkumbini	Albania	Paper	1960	1960	1990	35	(3)	-33.6
ADR	Semani	Albania	Ura Vajgurore	2070	1960	1989	33	(3)	-29.4
ADR	Vijose	Albania	Dorze	5420	1965	1984	145	(5)	--
AEG	Axios	Greece	Konitsa	24700	1964	1986	24	(3)	--
ION	Acheloos	Greece	Avleko	5540	1965	1995	51	(3)	-30.2
AEG	Aliakmon	Greece	Il Arion	9500	1963	1987	50	(3)	--
AEG	Vadar	Greece	Skopje	4650	1961	1998	58	(3)	-47.1
AEG	Nestos	Greece	Temenos	5740	1966	1995	40	(3)	-54.8
NLE	Ceyhan	Turkey	Misis	20466	1971	1983	222	(5)	--
NLE	Dhiarizos	Cyprus	Philousa		1965	1994	2	(3)	--
NLE	Peristerona	Cyprus	Panayia Bridge	80	1965	1994	1	(3)	--

(1) See Table 1.1 (chapter I)
(2) No value means that trends were not significant at $P \leq 0.05$
(3) Medhycos (2001)
(4) Stucky (2001)
(5) Vörösmarty et al. (1998)

2.4 – Regional water budgets

The above-presented trends allow evidencing the relative changes of river inputs to the Mediterranean over time. But the data are not sufficient to establish regional water budgets. In order to translate these data into absolute values, a reliable estimate for the overall amount of freshwater inputs at a given time is needed. We retained for this purpose the water budget of Collectif (1978) that has been established in the framework of the UNEP MEDX programme. It distinguishes the water input into the Mediterranean with respect to its ten sub-basins (table 2.4), and results in an overall water input of about 440 km^3/yr. This value is close to other estimates found in the literature, such as those of Tixeront (1970) or of Margat (1992). In preparation of the new edition of the Blue Plan Book of the UNEP MAP programme, the latter author established a detailed water budget with respect to the different Mediterranean countries (Margat, in press), resulting in a total riverine freshwater input of about 430 km^3/yr. These values are shown for comparison in table 2.5. Also at a more regional scale, both water budgets are in very good agreement.

The Adriatic Sea is the sub-basin that receives the greatest amount of terrestrial runoff: more than one third of the overall freshwater input enters the Mediterranean Sea in this sub-basin. By far most of the water comes from Italy, the country with the highest contribution. The budgets of Margat (tabl. 2.5) also allow us to conclude that the groundwater discharge to the Mediterranean may represent an additional freshwater contribution of about 10% of the river discharge. The water loss due to direct evaporation of the water bodies is also in the range of 10% of the river discharge, with about one third related to the evaporation from water dams (mainly the Aswan dam in Egypt). When compared to the difference between precipitation and evaporation (P-ETR), it can be noticed that almost one fifth of the water resources (90 km^3/yr) are affected by anthropogenic water consumption.

We considered for our purpose that the water budgets presented above correspond more or less to the situation around 1970 (Collectif, 1978). They are already affected by major human impacts such as the damming of the Nile at Aswan, but do not reflect the further reduction in discharge during more recent years. This allows us to extend the water budgets to the beginning and to the end of the last century (Q-20 and Q-95, respectively) by applying the results of our trend analyses to the entire budgets. In table 2.4 we attributed to each of the terms of the sub-basin budgets a percentage of the estimated change in water discharge when going back to the beginning, and when going forward to the end of the 20th century (d-Q20 and d-Q95, respectively). The river examples that conducted us in the selection of these values are shown as well. Changes in precipitation were naturally considered in all cases, even if this is not always explicitly mentioned.

***Tab. 2.4** - Regional freshwater inputs to the Mediterranean by rivers at the beginning (Q-20), around 1970 (Q-70), and at the end of the 20th century (Q-95). For further explication, see text.*

Basin	Country	A 10^3 km^2	Q-70 km^3/yr	A 10^3 km^2	Q-70 km^3/yr	d-Q20 %	extrapolation according to	d-Q95 %	extrapolation according to	Q-20 km^3/yr	Q-95 km^3/yr
ALB	Spain	18.4	2.2	102	6	30.0	Ebro, P	-75.0	Moulouya, P	8	2
	Morocco	63.0	3.4			20.0	Moulouya	-75.0	Moulouya, P		
	Algeria	20.5	0.6			20.0	Moulouya	-75.0	Moulouya, P		
NWE	Spain	145.0	22.1	277	95	40.0	Ebro	-45.0	Ebro	114	80
	France	125.0	65.6			10.0	Rhone, Arno	-5.0	Rhone, Arno		
	Italy	7.4	7.3			50.0	Arno	-20.0	Arno, Tiber		
SWE	Algeria	79.0	3.7	115	9	20.0	Moulouya, Medjerdah	-15.0	Medjerdah	12	7
	Tunisia	2.2	0.1			20.0	Moulouya, Medjerdah	-15.0	Medjerdah		
	Italy	14.9	4.4			30.0	Moulouya, Medjerdah, P	-25.0	Tiber		
	Spain	18.6	0.9			40.0	Ebro	-45.0	Ebro		
TYR	France	6.4	3.0	87	39	50.0	Arno	-20.0	Arno	47	29
	Italy (Sard.)	9.2	2.7			20.0	Tiber	-25.0	Tiber		
	Italy	66.7	32.0			20.0	Tiber	-25.0	Tiber		
	Italy (Sicily)	5.0	0.9			20.0	Tiber	-25.0	Tiber		
ADR	Italy	154.3	98.3	231	164	22.5	Po, Adige, Pescara	-7.5	Po, Adige, Pescara	203	136
	Former Yugosl.	55.0	46.1			25.0	Pescara, P	-30.0	Krka, other Croatian		
	Albania	21.3	19.5			25.0	Pescara, P	-35.0	Shkumbini, other Albanian		
ION	Italy	23.0	9.1	52	35	25.0	Pescara, Ofanto, P	-35.0	Ofanto	44	23
	Italy (Sicily)	7.0	1.1			25.0	Pescara, Ofanto, P	-35.0	Ofanto		
	Albania	9.1	8.3			25.0	Pescara, Ofanto, P	-35.0	Shkumbini, other Albanian		
	Greece	12.6	16.3			25.0	Pescara, Ofanto, P	-30.0	Acheloos		
CEN	Tunisia	32.2	1.0	46	3	30.0	Ofanto, P	-35.0	Ofanto	4	2
	Italy	13.7	2.3			30.0	Ofanto, P	-35.0	Ofanto		
AEG	Greece	146.0	30.9	215	47	30.0	P, Ofanto	-50.0	Nestos, other Greek	61	23
	Greece (Crete)	9.1	1.4			30.0	P, Ofanto	-50.0	Nestos, other Greek		
	Turkey	60.3	14.5			30.0	P, Ofanto	-50.0	Nestos, other Greek		
NLE	Turkey	93.4	22.4	108	25	35.0	P, Ofanto	-10.0	Cyprian, P	33	22
	Cyprus	9.1	1.4			35.0	P, Ofanto	-10.0	Cyprian, P		
	Syria	5.7	0.7			35.0	P, Ofanto	-10.0	Cyprian, P		
SLE	Libya	7.3	0.8	2941	17	35.0	P, Ofanto	0.0	P	81	8
	Israel	10.3	0.3			35.0	P, Ofanto	0.0	P		
	Greece	3.3	0.5			35.0	P, Ofanto	0.0	P		
	Egypt	2920	15.8			400.0	Nile	-60.0	Nile		
	TOTAL			**4174**	**440**		**TOTAL**			**606**	**333**

Sources: column 1-6, Collectif (1978);
others: this study; d-Q20 and d-Q95 are the estimates differences in water discharge with respect to the water discharge in 1970. On the basis of these values, Q-20 and Q-95 were estimated.

Our approach brings us to the conclusion that the freshwater discharge to the Mediterranean by rivers is actually only about 330 km^3/yr compared to about 600 km^3/yr at the beginning of the last century. A direct comparison of our values with other independently derived literature estimates is possible with the work of Boukthir and Barnier (2000), who established a riverine freshwater budget for the entire Mediterranean for the period of 1974-1994. They found a value of about 350 km^3/yr. Taking 1984 as reference year for this value, and interpolating linearly our estimates for Q-70 and Q-95 to this year gives a freshwater discharge of about 375 km^3/yr, which is in good agreement with the first value. One may also mention here that the overall discharge estimated from the drainage intensity maps of Korzoun et al. (1977; see also chapter I) is about 590 km^3/yr (140 for the western basin, 450 for the eastern basin). This is indicating that their work rather reflects the situation at the beginning of the 20th century. But it is also possible that these values are somewhat too high. Summing up values for drainage intensity from maps on a grid point scale tends to overestimate the real values since this cannot account for water losses due to evaporation and anthropogenic water extraction.

On the level of the Mediterranean sub-basins, the evolution of freshwater discharge over time is more diverse (fig. 2.5). The most striking feature is naturally the reduction of the inputs to the South-Levantine Sea due to the damming of the Nile. The actual value is only about 5-10% of the original one at the beginning of the last century. In reality, this may be still an overestimation. Due to the irrigation practices in the Nile delta, where water use is very intense and much water is directly discharged to the sea from the fields, is almost impossible to obtain reliable figures. We retained the value of 6 km^3/yr of Abdel-Moati (1999) for the actual Nile discharge, which is close to the 4.5 km^3/yr that were originally fixed by the Egypt water authorities as minimal discharge (Kempe, 1993). But it is possible that this value is actually not respected, not at least also because of the severe precipitation decrease in the Nile basin since the sixties (see above), which might have considerably increased the water stress in the basin.

Otherwise it is remarkable that the Q-20 to Q-70 evolution is rather uniform in the different sub-basins. The reduction towards the seventies is almost everywhere in the range of 20-30%. More severe reductions such as in the Ebro and/or Arno rivers are compensated by the more or less constant discharge of the Rhone or the Po rivers. The Q-70 to Q-95 evolution, however, is more variable, and the general trend of a decrease of the freshwater inputs is accelerated. The overall reduction is in the range of 110 km^3/yr, compared to about 170 km^3/yr for the Q-20 to Q-70 time span, although the latter period is about twice as long and strongly impacted by the closure of the Aswan dam. During the more recent years, the North-Levantine, the Northwestern and the Adriatic basins are the less affected by the reduction (about 10 to 20%), whereas the drop is more pronounced in the Tyrrhenian, Ionian and Aegean basins (about 25 to 50%). With an estimated reduction of about 75%, the Alboran Sea encounters the strongest reduction.

Tab. 2.5 - *Regional freshwater inputs to the Mediterranean according to Margat (in press)*

Countries	Precipitation	Resources and fluxes						Present fluxes going out of countries					Consumption and losses	
	1	2	3	3'	4	4'	5	6	7	8	9	9'	10	11
	Yearly Average Precipitation P	Internal Resources of Countries (P-ETR)	Groundwater (2-3')	Surface water resources (2-3)	External Contribution from neighbouring countries (surface water and ground water)	Contribution from non Mediterranean countries (included in 4)	Total Resources (2+4')	Real Rivers discharges toward the Mediterranean sea	Groundwater fluxes toward the Mediterranean	Real discharges towards the neighbouring countries	Discharges flowing out from countries (6+7+8)	Discharges flowing toward the Mediterranean (6+7)	Final Consumption by users including effluents in the sea	Losses by evaporation of dams
Spain	112.00	28.00	10.44	17.56	0.35	0.10	28.10	14.30	0.65	0.03	14.98	14.95	10.25	1.00
France	123.00	64.00	32.00	32.00	8.50	8.50	72.50	66.00	0.20	0.70	66.90	66.20	5.00	0.30
Italy	296.00	182.50	43.00	139.50	6.30	2.00	184.50	155.10	12.00	0.00	167.10	167.10	18.00	
Malta	0.17	0.05	0.05	0.00	0.00		0.05	0.00	0.04	0.00	0.04	0.04	0.03	
Slovenia	6.54	4.21		4.21	0.00		4.21	0.25	0.15	3.80	4.20	0.40	0.00	
Croatia	26.50	18.00	9.00	9.00	13.70		18.00	21.20	10.50	0.00	31.70	31.70	0.50	
Bosnia-Herzegovina	22.00	14.00		14.00	0.00		14.00	0.02	0.05	13.58	13.65	0.07	0.04	
Yugoslavia	22.00	16.00	2.00	14.00	0.00		16.00	1.50	1.60	12.00	15.10	3.10	0.27	
FYR Macedonia	18.00	5.42		5.42	1.00		5.42	0.00	0.00	6.30	6.30	0.00	0.77	
Albania	42.70	26.90	6.20	20.70	15.90	2.00	28.90	40.70	1.00	0.00	41.70	41.70	0.60	
Greece	113.40	58.00	10.30	47.70	11.20	10.20	68.20	48.70	2.50	2.00	53.20	51.20	6.00	1.00
Turkey	140.00	66.00	20.00	46.00	3.45	2.80	68.80	50.00	12.00	0.20	62.20	62.00	6.00	
Cyprus	4.42	0.78	0.28	0.50	0.00		0.78	0.18	0.23	0.00	0.41	0.41	0.17	
Syria	13.55	5.00	2.38	2.62	0.83		5.00	1.33	1.00	0.85	3.18	2.33	1.60	0.50
Lebanon	8.20	4.60	3.10	1.50	0.00		4.60	2.00	0.72	0.64	3.36	2.72	1.00	
Israel	3.00	0.63	0.45	0.18	0.38		0.63	0.00	0.00	0.01	0.01	0.00	1.00	0.12
Palestinian Authority	1.42	0.62	0.55	0.07	0.01		0.62	0.02	0.00	0.50	0.52	0.02	0.13	0.00
Egypt	12.00	0.80	0.50	0.30	55.50	55.50	56.30	13.00	0.03	0.00	13.03	13.03	35.10	10.00
Libia	10.00	0.70	0.60	0.10	0.00		0.70	0.05	0.05	0.00	0.10	0.10	0.50	
Tunisia	33.00	3.70	1.15	2.55	0.32		3.70	0.65	0.20	0.00	0.85	0.85	1.10	0.47
Algeria	68.50	14.50	1.33	13.17	0.03		14.50	11.30	0.00	0.32	11.62	11.30	1.70	
Morocco	21.00	5.00	1.00	4.00	0.00		5.00	3.65	0.10	0.03	3.78	3.75	0.90	
Total	1098.00	519.00	144.00	376.00	117.00	81.10	600.10	430.00	43.50	41.00	514.50	473.50	90.00	13.40

* The water resources of the Mediterranean countries are 600 km^3 including 81 km^3 coming from the upstream countries.

* The consumption related to the uses makes up 90 km^3.

* The river discharges flowing to the Mediterranean make up 473.5 km^3 : 430 km^3 of surface water, 43.5 km3 of underground water.

* Evaporation from surface water make up around 46.5 km^3; the thrird is related to the evaporation from water dams.

It is evident that it cannot be always guaranteed that the examples we selected to extrapolate our budgets were really representative for an entire region, leaving some uncertainty about the given values. Another problem is the scarceness of river records in certain regions, such as Turkey. Nevertheless, the general agreement at regional scales between individual river records, and between river discharge and precipitation records, suggest that our values might be quite close to reality, at least as far as the relative changes are concerned. Italian rivers are best represented in our data, and given the importance of these rivers in the overall water flow, this alone might give some robustness to our data.

One has therefore to keep in mind that the riverine freshwater inputs to the Mediterranean might actually only represent about 55% of what they were at the beginning of the 20th century. It is not excluded that this had some impact on the functioning of the marine system. Of course, it is not clear whether this trend actually holds on. More recent data are needed to answer this. But when looking at the evolution of rainfall (fig. 2.2), it is indicated that the evolution rather tends towards more humid conditions again.

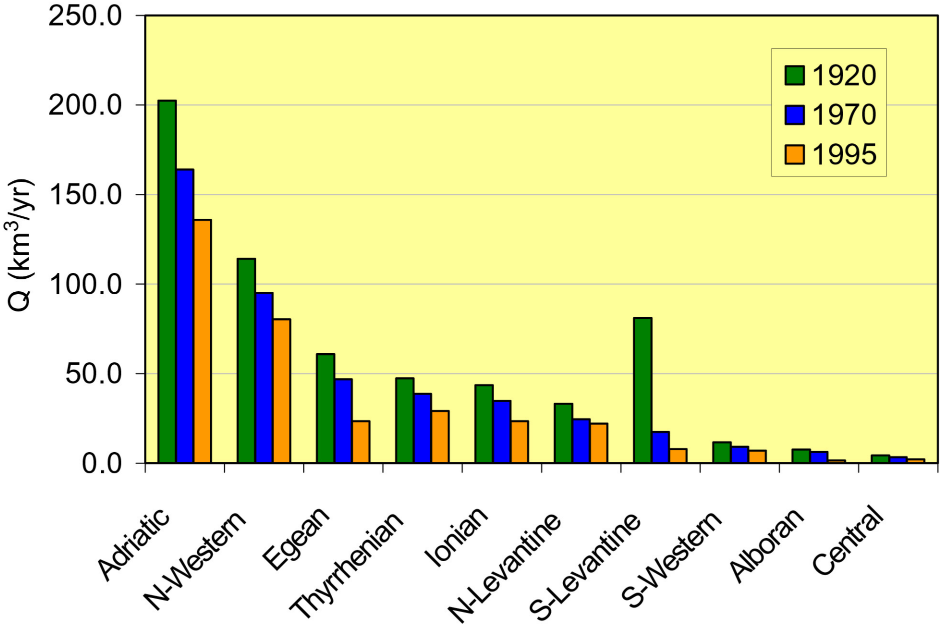

Fig. 2.4 *- Estimated changes in the riverine freshwater inputs to the Mediterranean during the 20th century*

Finally, it is also worth being pointed out that the two largest northern rivers, the Rhone and the Po rivers, do not follow the general trend. Despite marked interannual and decadal fluctuations, their average discharge remained more or less constant. This means that their relative importance in the overall supply of terrestrial matter to the sea increased. Both rivers together account actually for about 31% of the total water discharge to the Mediterranean, whereas this was only about 17% at the beginning of the last century.

Chapter III – Sediment fluxes

3.1 - Introduction

River sediment fluxes to the sea play an important role in various natural geochemical cycles such as the global carbon cycle. Also the transport and cycling of human released pollutants is often strongly coupled to the transport of sediments in rivers, since many contaminants are strongly associated with the particulate phase in water. Modern changes in drainage basin characteristics, such as river damming, extensive agriculture and/ or the broad construction of buildings and roads can highly alter natural erosion rates and river sediment transport. Such perturbations may have severe consequences for the land use, through the loss of fertile soils, or for the geomorphologic evolution of the riverbeds. But also in the estuaries and coastal zones, where sediments end up, an alteration of the natural river sediment supply can provoke considerable changes of the coastal metabolism, the biogeochemical cycling, or the coastline morphology.

Because of the strong seasonality of climate, the presence of elevated mountain ranges, the wide dominance of younger, softer rocks, and a long history of human activity, Mediterranean rivers tend to have high values of natural sediment fluxes (Milliman, 2001). At the same time, the warm and dry climate makes that anthropogenic pressure on the water resources is great, and human perturbations may have had more severe consequences on the natural fluxes than in other regions of the world. An assessment of the evolution of the river sediment delivery over time is therefore one of the crucial tasks in order to evaluate the impact of rivers on the biogeochemical and hydrosedimentological functioning of the Mediterranean Sea.

3.2 – Flux calculations

Calculating average values that are representative for a particular river is much more difficult for the fluxes of particulate solids than for the fluxes of dissolved solids. In many rivers, the variability of the concentrations of total suspended solids (TSS) is greater than the variability of water discharge. Both parameters do not evolve independently, and an increase of discharge is generally accompanied by an increase of concentrations. But the relationships are normally not that simple, and a determination of reliable fluxes requires a high sampling frequency during peak discharges. Most of the sediment discharge occurs during floods, which are brief and violent in the Mediterranean area, and which are difficult to be monitored. Moreover, the occurrence of strong floods is very irregular over time, which implies that the inter-annual variability of river sediment fluxes can be very important, too. Monitoring a particular river during a few years is not necessarily representative for the long-term average sediment transport in this river, even if the monitoring has been carried out under optimal conditions.

3.2.1 – Seasonal variability and sampling frequency

The Rhone River is one good example where the effect of sampling frequency on the result of flux calculations can be studied. This river has been monitored in a daily sampling frequency over several years (Pont, 1997; Pont et al., 2002), leading in a very complete data set of daily concentrations and daily discharge values for at least one hydrological year. By chance, this period also covered an important flood with a recurrence period of once every 30 years.

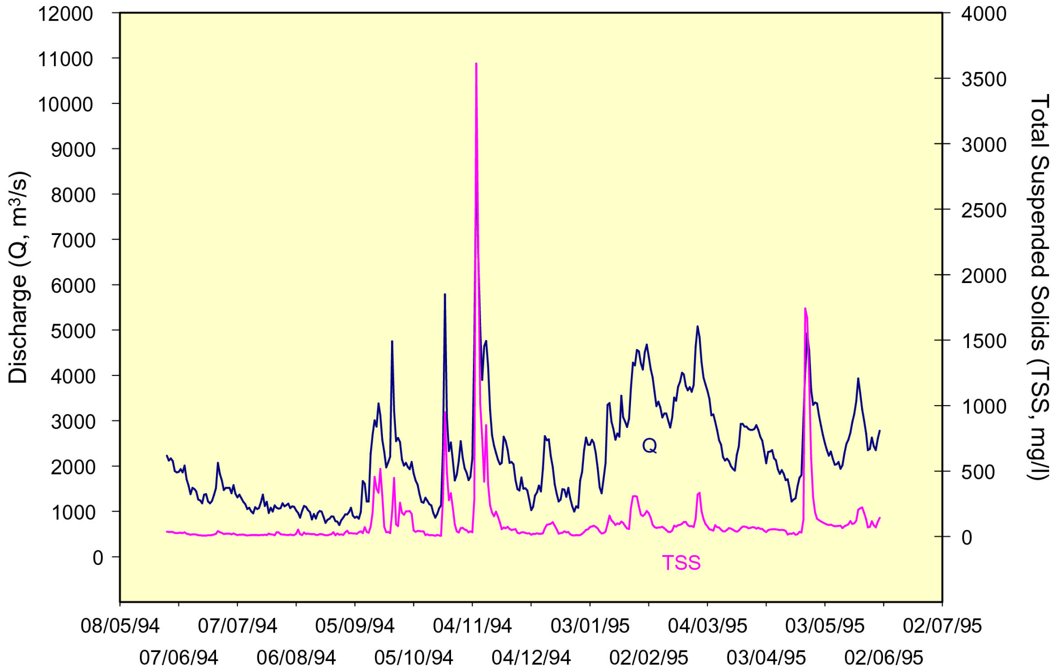

Fig. 3.1 *- Evolution of daily discharge and daily TSS concentrations in the Rhone from June 1994 to June 1995 is shown (data from the courtesy of D. Pont, and from Medhycos, 2001).*

The evolution of daily discharge and daily TSS concentrations in the Rhone from June 1994 to June 1995 is shown in figure 3.1 (data from the courtesy of D. Pont for TSS concentrations, and from Medhycos (2001) for Q). Discharge varied from about 700 to 8860 m^3/s (geometric mean: 2070 m^3/s), and TSS concentrations from 6 to 3612 mg/l (geometric mean: 50 mg/l). Note that the min/max concentrations varied with a factor of about 600, whereas daily discharge only varied with a factor of about 13!

With the above-presented data set, a reliable total sediment flux can be calculated by adding the daily fluxes during the year of observation. This corresponds to the method C in table 3.1, which summarises the most currently applied methods for the calculation of mean annual river fluxes. The overall sediment flux was hence about 14.2 Mt/yr (tab. 3.2), with a corresponding water flux of 70.1 km^3/yr. Since the sampling was completely regular on a daily basis, the method B, based on the determination of the discharge-weighted average TSS concentration, yields exactly the same value. Method D, which is probably the most frequently applied method in the determination of river sediment fluxes (although the correction according to Ferguson (1986, 1987) is often omitted), yields a value that is about 11% lower. The worst method is method A. This method should be avoided in all cases where the evolution of concentrations is not independent from the evolution of discharge.

Table 3.1 *- Currently applied methods for the calculation of mean annual river fluxes*

(i) $C_{av}=\frac{\sum_{i=1}^{n} C_i}{n}$ (ii) $F_{annual}=C_{av}\times Q_{annual}$	A - Arithmetic mean: Calculation of an average concentration (C_{av}) on the basis of n samples of instantaneous concentrations (C_i), and multiplication with an estimate for the annual discharge total (Q_{annual}).
(i) $C_{dw}=\frac{\sum_{i=1}^{n} C_i\times Q_i}{\sum_{i=1}^{n} Q_i}$ (ii) $F_{annual}=C_{dw}\times Q_{annual}$	B - Discharge weighted mean: As A, but calculation of a discharge weighted mean concentration (C_{dw}) on the basis of n samples of instantaneous concentrations (C_i) and instantaneous discharge values (Q_i)
(i) $C_j=\frac{\sum_{i}^{i+1} C_i\times Q_i}{\sum_{i}^{i+1} Q_i}$ (ii) $F_{annual}=\sum_{j=1}^{m} C_j\times Q_j$	C - Partial Fluxes: Calculation of a discharge weighted mean concentration for each period j between to sampling events (C_j). Multiplication of this concentration with the total discharge corresponding to this period (Q_j) and summing the fluxes of the m periods covering one hydrological year ($m = n - 1$).
(i) $\log(C_i)=a\times\log(Q_i)+b$ $\log(C_i)=a\times\log(Q_i)^2+b\times\log(Q_i)+c$ . . . (ii) $F^*_{annual}=\sum_{d=1}^{365} C_{th-d}\times Q_d$ (iii) $s^2=\sum_{i=1}^{n}\frac{\log(C_i)-\log(C_{i-th})}{n-2}$ (iv) $c_f=\exp(2.651\times s^2)$ (v) $F_{annual}=F^*_{annual}\times c_f$	D - Regression model: Determination of an empirical regression model between instantaneous concentrations and discharge values (often in logarithmic form). Calculation of a theoretical daily concentration (C_{th-d}) and multiplication of theses values with daily discharge for all days of the year. In the case of logarithmic relationships with large scatter, this method tends to underestimate real fluxes and should be corrected according the method proposed by Ferguson (1986, 1987).

In reality, daily sampling of water quality parameters in rivers is costly and difficult to realize. Most monitoring surveys are based on a less frequent sampling in regular time steps, and the results of the flux calculations are highly sensitive to the number and temporal distribution of the sampling events. To demonstrate this, we also present in table 3.2 the results of the flux calculations when the survey would have been done in weekly time steps. We assumed that the sampling was perfectly regular, and always carried out during the same day in the week (every Monday, every Tuesday, and so on). The calculations were repeated seven times by always choosing another day in the week for sampling (the first and last sampling days were always maintained in order to keep the corresponding annual water discharge unchanged). One can notice that simply the fact of changing the sampling day in the week provokes a variability of the resulting annual flux with a factor of about 2-3 in all calculation methods!

***Table 3.2** - Sediment fluxes (Mt/yr) in the Rhone River at Arles from June 1994 to June 1995 when calculated with the different methods of table 3.1 (for further explication, see text).*

	Method for flux calculation			
sampling	A	B	C	D
daily	8.0	14.2	14.2	12.6
weekly-1	6.5	9.2	9.9	13.5
weekly-2	6.0	8.1	8.4	11.4
weekly-3	6.9	11.1	10.5	11.9
weekly-4	6.1	8.4	8.2	8.9
weekly-5	12.4	28.9	23.9	13.9
weekly-6	9.9	19.5	18.4	16.4
weekly-7	7.6	12.1	12.6	14.5
average	7.9	13.9	13.1	12.9
std-dev.	2.4	7.7	5.9	2.4
std-dev. (%)	29.9	55.4	44.6	18.8
max	12.4	28.9	23.9	16.4
min	6.0	8.1	8.2	8.9
max/min	2.1	3.6	2.9	1.8

A weekly sampling is a rather high frequency and most surveys are even less frequent. National monitoring agencies, such as the “Agence de l’Eau” in France, normally sample only one time a month. It is easy to imagine that this is not necessarily meaningful for the determination of annual river sediment fluxes.

3.2.2 – Long-term variability

Establishing empirical relationships between TSS concentrations and discharge (method D in table 3.2) has one advantage compared to the other methods. These so-called rating curves can be applied to longer times series of discharge records in order to investigate the inter-annual variability of the fluxes. For this purpose, we applied the rating curve for the Rhone River (fig. 3.2a) to the daily discharge record from 1980 to 1999 (a twenty-year period corresponds about to the frequency of the long-term fluctuations of the rivers discharge - see chapter II). This results in annual fluxes that vary within one order of magnitude (from about 2.4 to 25 Mt/yr), with an average long-term mean of 8.5 Mt/yr). The corresponding water discharge varies only by a factor of two, from about 34 to 68 km^3/yr (average: 55 km^3/yr).

However, it would be misleading to take this variability as representative for other rivers of the Mediterranean area. Because of its relative large basin size, and because of its headwaters coming from the temperate climate in the north, the Rhone is not a typical Mediterranean river. Water discharge is rather regular compared to the basins that are entirely under the influence of the Mediterranean climate.

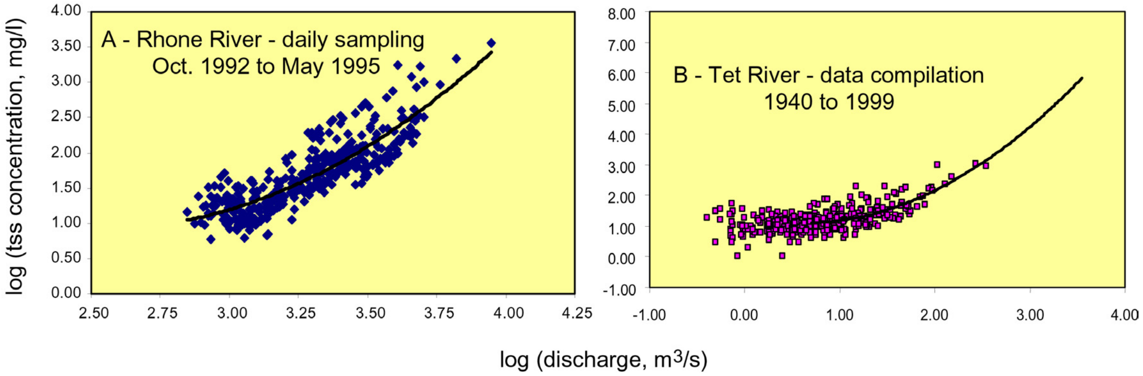

Fig. 3.2 *- TSS - Q rating curves of the Rhone (a) and the Tet (b) rivers in southern France*

The Tet River in the southwestern corner of the French Mediterranean coast is a small Mediterranean river that is more typical in this respect. Also for this river, the inter-annual variability of the river sediment discharge was investigated for the 1980 to 1999 period by Serrat et al. (2001). The rating curve for this river is shown in figure 3.2b. The authors found a mean annual sediment flux of about 0.05 Mt/yr for the Tet River, corresponding to a sediment yield (sediment flux divided by basin area) of less than 50 t/km^2/yr. This average value is rather low compared to other Mediterranean rivers (see below), which might be explained by the rather old and hard rocks in the headwater regions of the river, together with the presence of an artificial reservoir in the lower part of the drainage basin. But when looking at individual years, the study revealed annual sediment fluxes ranging from about 0.001 to 0.350 Mt/yr, while the corresponding annual water discharge varied from about 0.07 to 0.7 km^3/yr. This underlines the extreme variability of the river sediment transport in the Tet River. According to Serrat et al. (2001), more than 50% of the overall sediment transport for the 20 years of investigation was discharged during only 13 days!

Also here, it becomes evident that estimates for the average sediment transport in rivers as the Tet River may easily result in different values, depending on whether the data would have been acquired during dry, normal and/or humid years. Only long-term surveys can ensure the determination of realistic average fluxes.

3.3 – Variability of natural sediment fluxes

Table 3.3 presents a compilation of estimates for river sediment yields for various Mediterranean rivers. They are “natural” values, which means that they refer to the conditions before the existence of major dams that were constructed in many of the river basins.

Table 3.3 *- River sediment yields for various Mediterranean rivers*

River	Area 10^3 km^2	sediment yield t km^{-2} y^{-1}	Sub-basin	Country	source
BUNA	5.2	486	ADR	Albania	96.027
DRINI	14.2	1173	ADR	Albania	96.027
ERZENI	0.8	9526	ADR	Albania	96.027
ISHMI	0.7	5899	ADR	Albania	96.027
MARTI	2.4	1037	ADR	Albania	96.027
OSUMI	2.0	2790	ADR	Albania	96.027
SEMANI	5.7	2000	ADR	Albania	96.027
SHKUMBINI	2.5	1910	ADR	Albania	96.027
VIJOSE	6.7	1251	ADR	Albania	96.027
CHELIFF	43.7	78	SWE	Algeria	76.126
ISSER	31.6	193	SWE	Algeria	84.209
KEBIR	1.1	200	SWE	Algeria	95.013
SEYBOUSSE	6.0	333	SWE	Algeria	95.013
SOUMMAM	8.0	513	SWE	Algeria	95.013
TAFNA	6.9	145	SWE	Algeria	95.013
NILE	2870.0	42	SLE	Egypt	92.009
RHONE	95.6	324	NWE	France	92.009
VAR	1.8	4094	NWE	France	76.126
ALIAKMON	9.2	461	AEG	Greece	97.019
AXIOS	24.7	1220	AEG	Greece	00.002
NESTOS	6.1	160	AEG	Greece	97.019
PINIOS	10.2	600	AEG	Greece	00.002
ACHELOOS	5.5	614	ION	Greece	97.019
ARACHTHOS	1.9	3941	ION	Greece	97.019
KALAMAS	1.8	1296	ION	Greece	97.019
OFANTO	2.7	666	ADR	Italy	74.036
PESCARA	3.1	297	ADR	Italy	95.013
METAURO	1.4	857	ADR	Italy	95.013
RENO	3.4	798	ADR	Italy	74.036
PO	70.0	217	ADR	Italy	69.061
BIFERNO	1.3	1730	ADR	Italy	74.036
ADIGE	12.0	133	ADR	Italy	78.162
SIMETO	1.8	1960	ION	Italy	74.036
CRATI	1.3	901	ION	Italy	95.013
BRADANO	2.7	1020	ION	Italy	74.036
ARNO	8.2	268	NWE	Italy	68.075
OMBRONE	2.6	731	TYR	Italy	95.013
TEVERE	16.6	453	TYR	Italy	68.061
VOLTURNO	5.5	764	TYR	Italy	95.013
MOULOUYA	51.0	250	ALB	Morocco	02.001
EBRO	84.0	214	NWE	Spain	92.009
MEDJERDA	21.8	963	SW	Tunisia	76.126
GOKSU	10.1	248	NLE	Turkey	92.009
CEYHAN	22.0	250	NLE	Turkey	95.013
SEYHAN	22.0	236	NLE	Turkey	95.013

For source indexes, see reference list

This does, of course, not mean that the values are necessarily free of any human impact. In fact, sediment fluxes in the Mediterranean rivers may have been affected by deforestation, mining, industrialisation and urbanisation for many centuries, or even millennia. Well-known examples are the Ebro and Po rivers, whose deltas prograded appreciably over the past centuries in response to increased deforestation in the upper parts of the respective river basins (Mariño, 1992; Sestini, 1992; Ibàñez et al., 1997 – fig. 3.3).

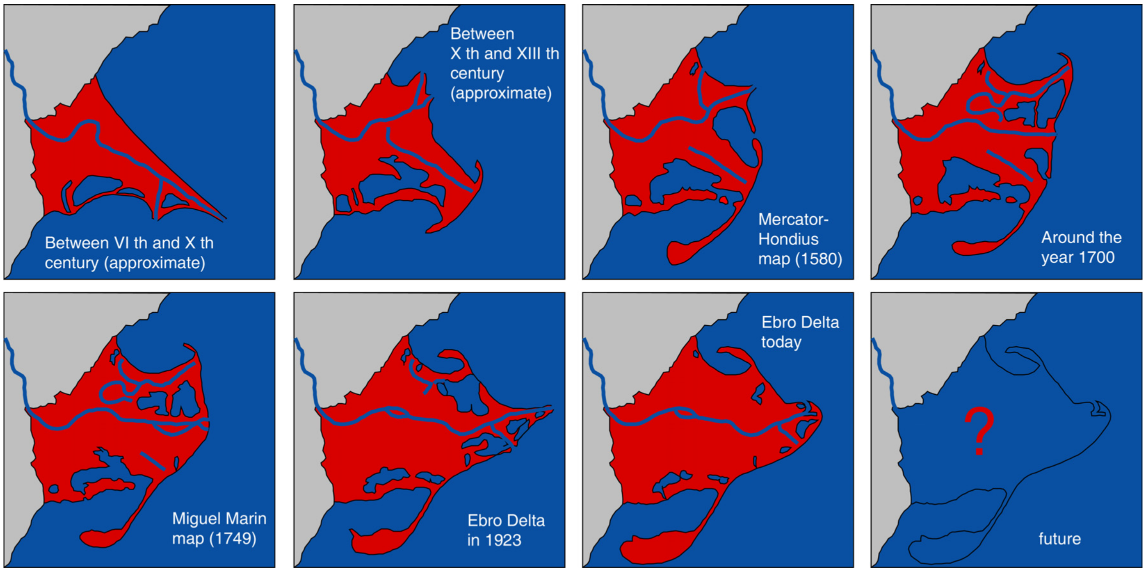

Fig. 3.3 *- Evolution of the Ebro delta during historical times (Ibàñez et al., 1997)*

The above-discussed difficulties in the determination of average sediment yields must be kept in mind when considering such a compilation of river data. Often, it is not clear how these values have been calculated, and the data should probably be taken as an order of magnitude estimate rather than as a precise value. Nevertheless, even if some of the values may be considered with caution, it has to be noticed that the Mediterranean rivers are generally characterized by very high sediment yields. Almost all rivers have values that are clearly above 150 – 200 t km^{-2} yr^{-1}, which is the world average for the ice-free and exoreic parts of the continents (Milliman and Meade, 1983; Milliman and Syvitski, 1992). For some rivers, sediment yields of several thousands of t km^{-2} yr^{-1} are reported, which are among the greatest values that are known for world rivers. Note that the Yellow River in China (or Huanghe River), which owns his name to his very high sediment load that provokes the characteristic yellow colour of the water, has an average sediment yield of “only” about 1400 t km^{-2} yr^{-1} (Milliman and Syvitski, 1992).

By far the greatest sediment yields are found for the rivers of Albania. It is here were the environmental conditions that are leading to high soil erosion rates and river sediment fluxes are unified: very high drainage intensities, steep slopes, strong seasonality of climate and the abundance of soft lithologies (fig. 3.4). For the same reasons, also in the Greek and Italian rivers that are discharging to the Ionian Sea, the values are very high. Further west, in the Western Mediterranean basin, sediment yields are generally lower. Drainage intensities and relief become less important, and older and harder rocks such as the Pyrenees may be dominant.

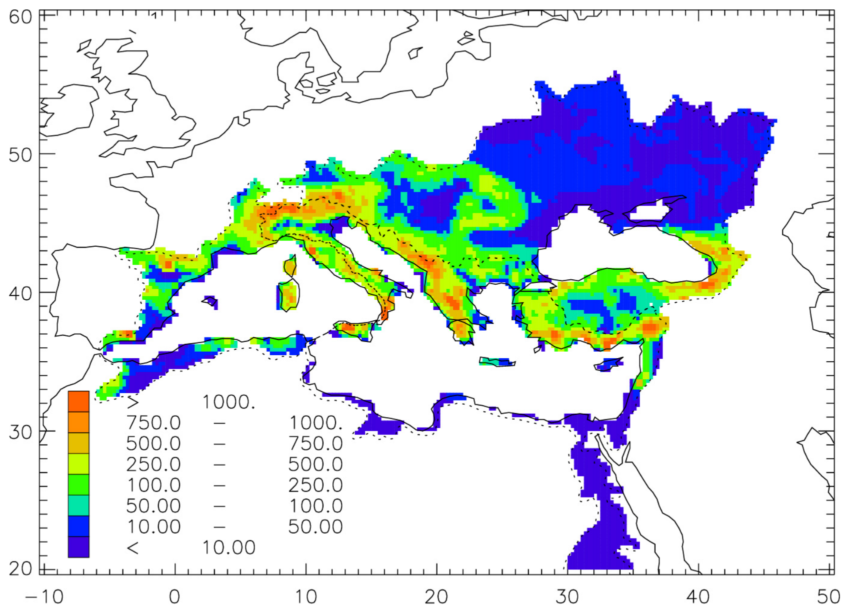

***Fig. 3.4** - Theoretical sediment yields as a function of the hydroclimatic, morphological and lithological characteristics of the Mediterranean and Black Sea drainage basins (adapted from Ludwig and Probst, 1998).*

Although the scatter between rivers of the same region can be great, some general trends emerge and one may use the values to establish a tentative budget for the natural sediment delivery to the Mediterranean Sea. For this purpose, we used the decomposition of the Mediterranean drainage basin according to the different countries and marine sub-basins of Collectif (1978; see also chapt. II) and assigned an estimate for the average sediment yields to each area in agreement with the data in table 3.3. This results in an overall sediment flux of 730 million tons per year (table 3.4). About 75% of the sediments enter the Mediterranean in its eastern basin, and 25% in the western basin. The sediment yield for the entire drainage basin, including the Nile, is about 175 t km^{-2} yr^{-1}, close to the global average. Excluding the Nile from the calculation increases the value to an average of about 580 t km^{-2} yr^{-1}, which is very high compared to other regions of the world (Ludwig and Probst, 1998).

In our assignment, we rather selected sediment yields towards the lower range of the documented values. A general problem in extrapolating sediment yields for individual rivers to larger scales is that it is normally not known were the gauging stations were situated to which the measurements correspond. In the headwater regions of river basins, sediment yields are normally much greater than further downstream (Milliman and Syvitski, 1992; Ludwig and Probst, 1998), and extrapolating these values the entire drainage basin often leads to an overestimation of the total sediment discharge for a given river. It is not excluded, however, that the values we estimated may be even greater in reality.

Table 3.4 *- Tentative budgets for the natural sediment delivery to the Mediterranean Sea*

Basin	Country	Area (1)	F_{TSS} (2)	F_{TSS} (3)	Area (1)	F_{TSS} (3)
ADR	Albania	21.3	1500	32	30	46
ION	Albania	9.1	1500	14		
ALB	Algeria	20.5	250	5	100	33
SWE	Algeria	79	350	28		
NLE	Cyprus	9.1	250	2	9	2
SLE	Egypt	2920	50	146	2920	146
NWE	France	125	350	44	131	47
TYR	France	6.4	500	3		
ION	Greece	12.6	1200	15	171	124
AEG	Greece	146	700	102		
AEG	Greece (Crete)	9.1	700	6		
SLE	Greece	3.3	200	1		
SLE	Israel	10.3	200	2	10	2
NWE	Italy	7.4	300	2	301	143
SWE	Italy	14.9	400	6		
TYR	Italy (Sard.)	9.2	550	5		
TYR	Italy	66.7	550	37		
TYR	Italy (Sicily)	5	550	3		
ADR	Italy	154.3	300	46		
ION	Italy	23	1200	28		
ION	Italy (Sicily)	7	1200	8		
CEN	Italy	13.7	550	8		
SLE	Libya	7.3	200	1	7	1
ALB	Morocco	63	250	16	63	16
ALB	Spain	18.4	200	4	182	38
NWE	Spain	145	200	29		
SWE	Spain	18.6	300	6		
NLE	Syria	5.7	250	1	6	1
SWE	Tunisia	2.2	950	2	34	20
CEN	Tunisia	32.2	550	18		
AEG	Turkey	60.3	700	42	154	66
NLE	Turkey	93.4	250	23		
ADR	Former Yugosl.	55	800	44	55	44
				total	4174	729

Basin	Country	Area (1)	F_{TSS} (2)	F_{TSS} (3)	Area (1)	F_{TSS} (3)
ADR	Albania	21.3	1500	32	231	122
ADR	Italy	154.3	300	46		
ADR	Former Yugosl.	55	800	44		
AEG	Grece	146	700	102	215	151
AEG	Greece (Crete)	9.1	700	6		
AEG	Turkey	60.3	700	42		
ALB	Algeria	20.5	250	5	102	25
ALB	Morocco	63	250	16		
ALB	Spain	18.4	200	4		
CEN	Italy	13.7	550	8	46	25
CEN	Tunisia	32.2	550	18		
ION	Albania	9.1	1500	14	52	65
ION	Greece	12.6	1200	15		
ION	Italy	23	1200	28		
ION	Italy	7	1200	8		
NLE	Cyprus	9.1	250	2	108	27
NLE	Syria	5.7	250	1		
NLE	Turkey	93.4	250	23		
NWE	France	125	350	44	277	75
NWE	Italy	7.4	300	2		
NWE	Spain	145	200	29		
SLE	Egypt	2920	50	146	2941	150
SLE	Greece	3.3	200	1		
SLE	Israel	10.3	200	2		
SLE	Libya	7.3	200	1		
SWE	Algeria	79	350	28	115	41
SWE	Italy	14.9	400	6		
SWE	Spain	18.6	300	6		
SWE	Tunisia	2.2	950	2		
TYR	France	6.4	500	3	87	48
TYR	Italy (Sard.)	9.2	550	5		
TYR	Italy	66.7	550	37		
TYR	Italy (Sicily)	5	550	3		
				total	4174	729

Units (1) = 10^3 km^2; (2) = t km^{-2} yr^{-1}; (3) = 10^6 t yr^{-1}

3.4 – Sediment retention in reservoirs

For many Mediterranean rivers, the building of dams in their respective drainage basins provoked a severe reduction in their sediment delivery to the sea (tab. 3.5). Before the closure of the Aswan High Dam, the Nile River alone carried on average about 120 Mt of sediments per year to the Mediterranean Sea (Kempe, 1993), representing thus more than 15% of the above-calculated budget for the entire Mediterranean basin. Today, the Nile's sediment transport seems to be less than 0.3 Mt/yr (Abdel-Moati, 1999). Another striking example is the Ebro River, where the sediment discharge decreased continuously during the last century in parallel with the increasing number of dam constructions in its drainage basin (fig. 3.5). Its actual sediment is probably less than 1% of its original value (Gullién and Palanques, 1992).

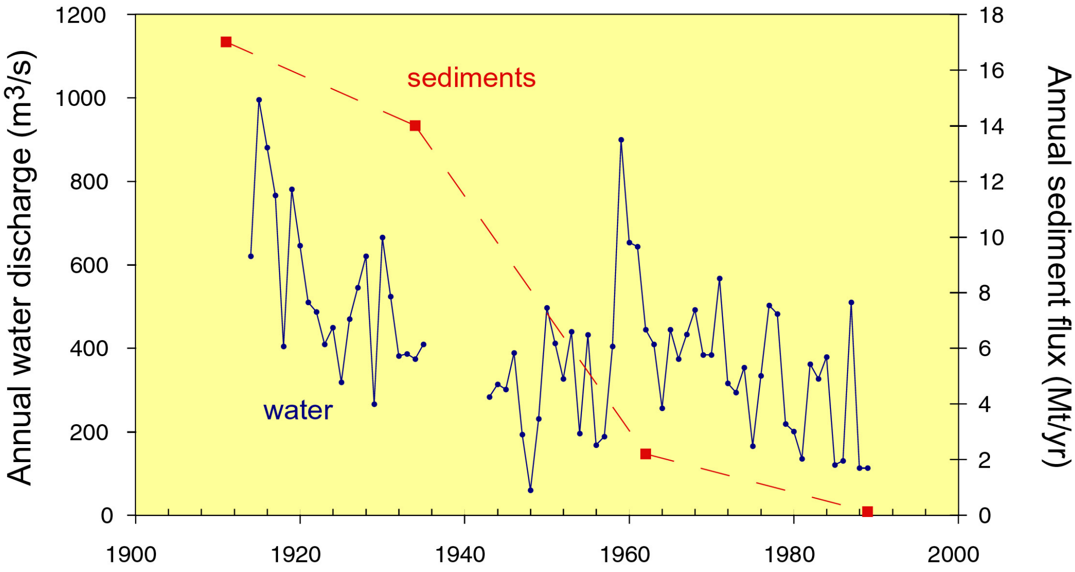

Fig. 3.5 *- Evolution of the water and sediment discharge in the Ebro River (from Gullién and Palanques, 1992)*

Unfortunately, direct measurements of the fluxes before and after the reservoir construction are rare, and most of the studies that attempted an evaluation the sediment trapping behind dams are based on indirect methods. A currently applied approach is to calculate the trapping efficiency as a function of the average annual residence time of the water in the reservoirs. The longer the water remains in the reservoir, the more particles settle down to the bottom and hence escape from the further downstream transport. Vörösmarty et al. (1997) found that a residence time of about 10 days is sufficient to retain 70% of the suspended particles in the river water (fig. 3.6). It is evident that this should have a major impact on the overall sediment transport to the Mediterranean Sea. Note that in 1997, the total reservoir capacities in France, Greece, Italy and Spain were about 12, 11, 11, and 52 km^3, respectively (Leonard and Crouzet, 1999). According to chapter II, this is about 19, 39, 8, and 394% of the total annual river discharge to the Mediterranean in these countries (for France and Spain, the reservoir capacities include also the rivers that are not flowing to the Mediterranean Sea).

Table 3.5 *- The impact of reservoir construction on the sediment fluxes in some Mediterranean rivers*

River	A Pre-damming sediment flux (Mt/yr)	Source A	B Actual sediment flux (Mt/yr)	Source B
Nile River	120	93.055	0.24	99.002
Rhone River	30	92.009	6-10	97.018, 00.001
Ebro River	17-25	92.065	0.12-0.15	92.065
Moulouya River	12	02.001	0.84	02.001
Tiber River	7.5	68.061	0.33	78.162

For source indexes, see reference list

Average residence times of river water in artificial reservoirs should therefore be at least several weeks when calculated on the basis of the global values for the above-mentioned countries. This implies trapping efficiencies of 80-90% and more. However, such an approach is naturally misleading in extrapolating real trapping efficiencies. Not all rivers of a country pass through reservoirs, while others are dammed several times along their courses. Dams are mostly constructed in the mountainous parts of the basins, leaving the downstream parts unaffected by reservoir retention.

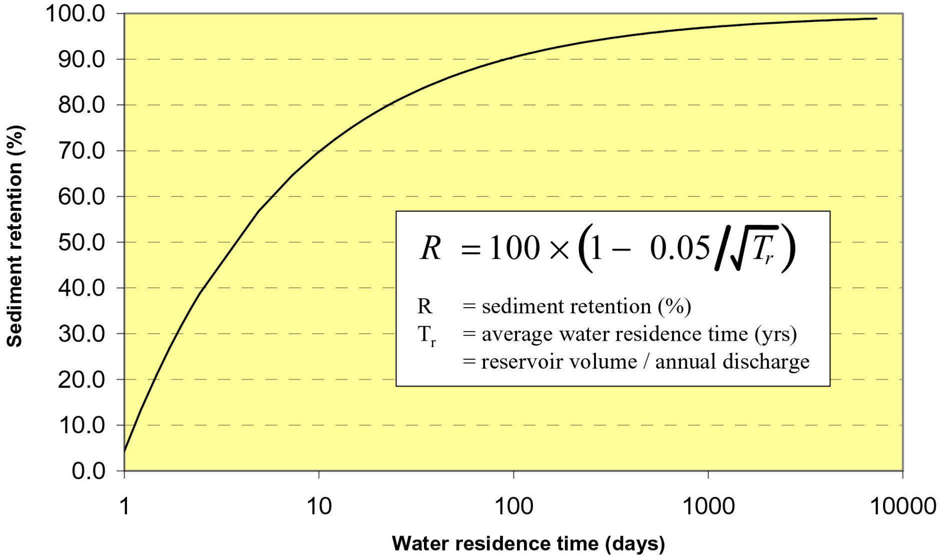

Fig. 3.6 *- Sediment trapping efficiency in reservoirs as a function of the average annual water residence time (Vörösmarty et al, 1997).*

When applying the relationship of Vörösmarty et al. (1997) to the Adour/ Dordogne / Garonne river system in the southwest of France, Maneux et al. (2001) calculated a trapping efficiency of about 30% for the entire river system. Sediment yields in this region are not very elevated, and higher erosion rates in the headwater regions may also be accompanied by greater sediment retentions for the entire basins. A sediment retention of about 60%, as indicated by the data for the Rhone River (tab. 3.5), may probably be more realistic for the Mediterranean rivers, at least in the northern part of the basin. Further south, trapping efficiencies should be greater because of the generally strong contrast in humidity between the upstream and downstream part of the basins.

Taking into account the almost complete stop of the sediment discharge of certain rivers such as the Nile and Ebro rivers, and generalizing the above-mentioned trapping efficiencies, we finally conclude that the overall reduction of the riverine sediment discharge to the Mediterranean Sea may be in the range of 75%. This means that probably only less than 200 Mt of sediments enter actually the marine realm every year. Much uncertainty is accompanied with this value, but the scarcity of data on this topic does not allow establishing more detailed estimates.

Chapter IV – Organic and bacteriological pollution

4.1 - Introduction

Organic pollution in rivers results from inputs of organic matter from various sources, such as household wastewater, industries (e.g. the paper industry or food processing industry), or silage effluent and slurry from agriculture. Bacteria decompose these organic materials using oxygen, thus reducing the dissolved oxygen content in the water. Severe organic pollution may therefore lead to rapid deoxygenation of river water, decreasing the oxygen concentrations down to levels that are harmful for of fish and aquatic invertebrates. Moreover, when the oxygen levels are low, ammonium often becomes the dominant inorganic nitrogen species (fig. 4.1), which can lead to high levels of un-ionised ammonia when the water temperature and pH values are great. Ammonia becomes toxic for aquatic animals at concentrations of 0.2 to 2 mg/l (Crouzet et al., 1999).

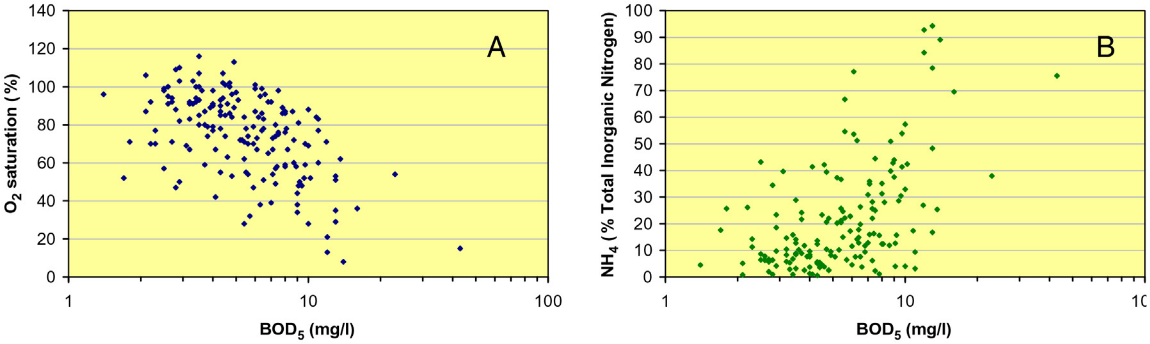

Fig. 4.1 *- (A) Relationship between BOD (mg/l) and oxygen saturation (saturation in %) and (B) BOD and ammonium content (as percent of total inorganic nitrogen (NO_3 + NO_2 + NH_4)) in the Tet River in southern France. The data is from the French monitoring Agency "Agence de l'Eau Rhône - Méditerranée - Corse" (http://www.rdbrmc.com/) and cover the period from 1982 to 1999.*

The amount of organic pollution in freshwater systems can be gauged by measuring the so-called biological oxygen demand (BOD). This is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions. BOD is determined by incubating a sealed sample of water for five days and measuring the loss of oxygen from the beginning to the end of the test (for this reason, it is often also abbreviated BOD_5). Alternatively, the chemical oxygen demand (COD) can be used to quantify organic pollution. The chemical oxygen demand does not differentiate between biologically available and inert organic matter, and is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. Also oxidizable inorganic matter contained in water may be measured and COD values are always greater than BOD values. COD is a laboratory test based on a chemical oxidant and, therefore, does not necessarily correlate with biochemical oxygen demand. The advantage is that COD measurements can be made in a few hours while BOD measurements take five days.

4.2 – Spatial variability of BOD levels

4.2.1 – World rivers

The BOD concentration of clean freshwater is normally around 2 mg/l, which is about the median value in world rivers (fig. 4.2). Values exceeding 5 mg/l indicate heavy pollution (Kristensen and Hansen, 1994). The figure 4.2 shows the statistical distribution of BOD in rivers of the different continents, corresponding to water quality data of approximately 175 stations in 82 major river basins for the period from 1976 to 1990 (Revenga et al., 2000). Although the BOD figures vary greatly, it can be seen that the highest concentrations were found in North America, in agreement with the highly developed industrial and agricultural activities in this part of the world. Values for Europe and Africa were also above the global median of 2 mg/l, whereas the lowest median is found for South America. It is probably here where many rivers are still close to a pristine state. Africa had a very wide range of values, which might be due to the absence of wastewater treatment in heavily populated areas of this continent, together with the dryness of climate. Also in Asia, wastewater treatment may be missing in some populated areas, but this may be partly compensated by greater drainage intensities.

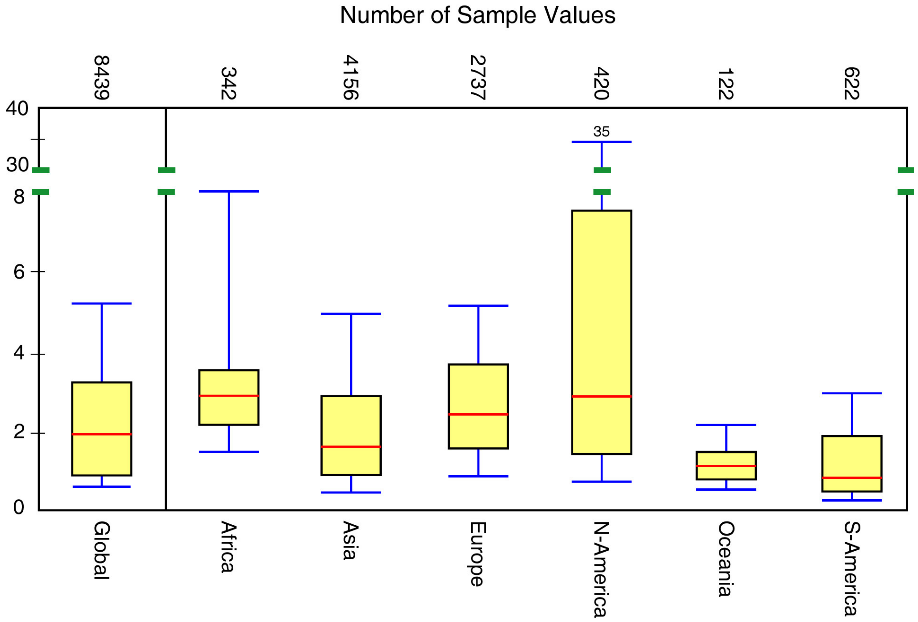

Fig. 4.2 *- Statistical distribution of BOD by continent (1976-1990). Data from Revenga et al., (2000). The red line represents the median value and the yellow boxes represent the 25th and 75th percentiles, respectively. The horizontal lines outside the boxes are the 10th and 90th percentiles, respectively.*

4.2.2 – Mediterranean rivers

A compilation of average BOD and COD values in different Mediterranean rivers is presented in table 4.1. In general, the values correspond to the most downstream stations of the drainage basins, close to the river mouths. For comparison, average values for the carbon content in these rivers obtained by direct measurements of the dissolved organic carbon (DOC) and particulate organic carbon

(POC) contents were added whenever this information was available. In some cases, only total organic carbon (TOC; TOC = DOC + POC) has been measured.

Table 4.1 *- Average BOD, COD, DOC, POC and TOC values in some Mediterranean rivers*

Rivers	BOD_5 mg/L	COD mg/L	*source*	period	DOC mg/L	POC mg/L	*source*	period	TOC mg/L	*source*	period
ADIGE	5.7	11.4	*97.007*	89-92					2.7	*95.017*	
AKHELOOS					1.1	0.3	*97.014*	83-84			
ALIAKMON					1.2	0.7	*97.014*	83-84			
ARGENS	3.5	10.0	*97.005*	85-96	2.4						
ARNO		32.3	*97.007*	89-92					6.1	*95.017*	
AUDE	3.1	15.0	*97.005*	85-96	3.3						
AXIOS					1.4	0.4	*97.014*	83-84			
BESOS	19.2	38.0	*97.010*	90-92							
BUYUK MENDERES		3.1	*97.015*								
CEYHAN	4.6	24.4	*97.015*								
EBRO	4.0	3.8	*97.007*	86-92	4.8	1.4	*89.180*	86-87			
EVROS					3.0	1.8	*97.014*	83-84			
FLUVIA	1.2	3.7	*97.010*	90-20							
GOKSU	1.5	22.2	*97.015*								
HERAULT	2.5		*97.005*	85-96	2.5		*97.005*	85-96			
KISHON	275.0	1700.0	*97.015*								
KRKA	2.5	9.7	*97.007*	90							
LLOBREGAT	5.3	15.3	*97.010*								
MANAVGAT	1.3	9.2	*97.015*								
MARTIL *	9.0		*97.020*	84-90							
METAURO		2.8	*97.007*	84-92							
MOULOUYA *	2.6		*97.020*	84-90							
NERETVA	2.0	9.8	*97.007*	78-90							
NESTOS	3.6	8.0	*94.064*	92-94	1.7	0.7	*97.014*	83-84	2.4		
NILE					3.5	4.4	*93.027*				
ORB	3.1		*97.005*	85-96	2.7		*97.005*	85-96			
PINIOS	4.0	3.8	*94.064*	92-94							
PO	7.0	18.1	*97.007*	82-92	2.6		*91.094*	88-90	4.7	*95.017*	
RHONE	1.5	5.0	*97.005*	85-96	2.6	5.2	*96.032*	94-95			
SEMANI	3.4	3.3	*97.007*	90							
SEYHAN	6.9	48.0	*97015*								
SHKUMBINI	5.2	3.7	*97.007*	90							
STRYMON					2.1		*97.014*	83-84			
TAVIGNANO	1.0		*97.005*	85-96	2.3		*97.005*	85-96			
TER	2.6	7.9	*97.010*	90-92							
TET	5.6		*97.005*	85-96	3.5		*97.005*	85-96			
TIBER	4.5	5.8	*97.007*	83-91					5.4	*91.081*	79-83
VAR	2.5	8.0	*97.005*	85-96	1.6		*97.005*	85-96			

* median value

For source indexes, see reference list

Since the values are not necessarily based upon the same number of measurements, and do not exactly refer to the same reference period, such a compilation has naturally to be considered with caution. There is also no single standardised system of water monitoring and assessment for surface waters in the different countries. In some cases, COD values are even lower that BOD values, which may be related to these difficulties.

Nevertheless, most of the BOD and COD values correspond to about the same period (e.g., 1985-1990), and we suppose that they still allow a general overview of the degree of organic pollution in the Mediterranean rivers. By far the strongest pollution is found in the Kishon River of Israel, which receives the wastewaters of Haifa and which is regarded to be the most polluted river in Israel (Herut and Kress, 1997). Also the Besos, Martil (a small coastal river in Morocco), Po, Seyhan, Adige, Arno, Tet Llobregat and Shkumbini rivers have to be considered as heavily polluted rivers, which is generally also related to the effluents of large urban agglomerations (such as for the Besos River, who receives the wastewaters of Barcelona in Spain). On the other hand, rivers with almost no or only weak pollutions are the Tavignano, Fluvia, Manavgat, Goksu, Rhone, Neretva, Krka, Herault and Var rivers.

The median BOD value of all rivers in table 4.1 is 3.5 mg/l. This is greater than the median value for European rivers in figure 4.2. EEA (1999) reported on the basis of information from about 1000 river sites across Europe that in the mid-1990s, 11% of the sites were heavily polluted, with average BOD values greater than 5 mg/l. But these pollutes sites were not uniformly distributed in Europe. In the Nordic countries and western Europe, only less than 10% of the sites had values above the 5 mg/l BOD limit, whereas this was around 25% for the rivers in southern and eastern Europe. Organic pollution in the Mediterranean region is therefore a greater problem than in the northern European countries. On the one hand, less money might be available in these countries for an improvement of wastewater treatment. On the other hand, the rather low drainage intensities in the Mediterranean area might lead to higher concentrations in rivers, even if the total wastewater inputs were comparable to other regions. The elevated temperatures also might reduce the auto-purification capacities in certain rivers.

Finally, it is interesting to compare the average BOD and COD concentration in table 4.1 with the average DOC and POC concentrations in the rivers for which these parameters have been determined independently. It is remarkable that, although BOD and COD are rather high compared to other world rivers, DOC and POC values are quite low. Whether the POC values are really representative for the indicated rivers is difficult to answer, because POC is normally closely coupled to the total suspended solids, and the difficulties in determining reliable averages for this parameter (see chapter 3) also holds for POC averages. DOC is generally less variable and the data should be more representative.

The median DOC concentration of the rivers in table 4.1 is 2.5 mg/l, whereas the average for world rivers is around 4-5 mg/l (Meybeck, 1982; Ludwig et al., 1996). DOC might largely reflect the organic compounds originating from the leaching of soil organic matter which are chemically rather inert and which are not necessarily available for rapid biological decomposition in the river waters. The riverine fluxes of dissolved organic carbon generally increase with increasing drainage intensities, flatter morphologies, and larger carbon reservoirs in the soils (Ludwig et al., 1996). Because of the steep morphologies, the often-low drainage intensities and the carbon poor soils in the Mediterranean area, it is therefore not surprising that DOC concentrations are generally low in these rivers.

4.3 – Temporal variability of BOD levels

Average values for BOD or COD alone may not be satisfactory for an evaluation of the risk of environmental damage related to organic pollution. It is also the variability of the values that has to be considered in this context. Even if the averages were moderate, it is possible that maximum values can be high enough to provoke irreversible damage in the fluvial ecosystems. The Mediterranean rivers are more vulnerable in this respect than the rivers of other regions because of the strong hydrological contrast between the dry and the wet seasons. Especially the small rivers draining the coastal regions are very dry in summer, and even relatively small amounts of urban and/ or agricultural wastewaters may be sufficient to cause environmental problems. Moreover, intense tourism in summer is often responsible for peak discharges of wastewaters in these regions, accentuating the seasonality of organic pollution. In France, many of the coastal rivers can therefore be temporarily affected by pollution although the BOD averages are not always very elevated (fig. 4.3).

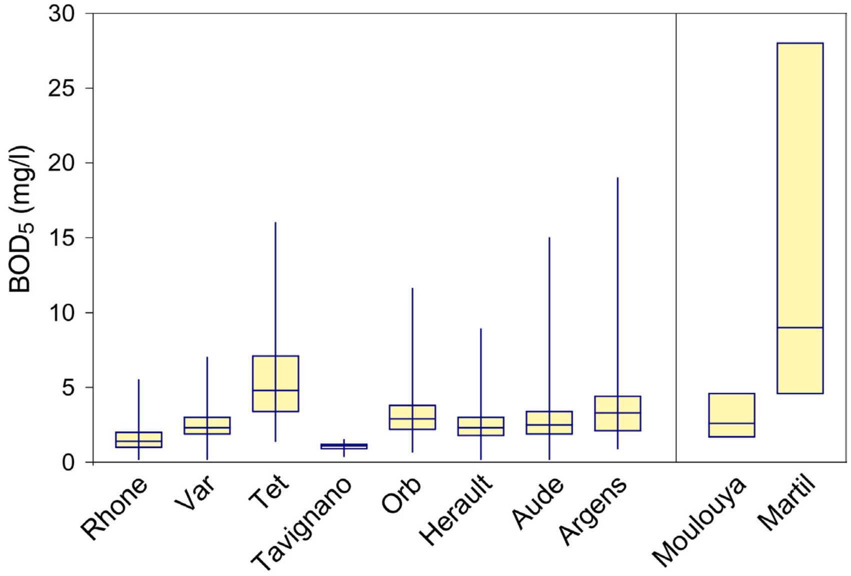

Fig. 4.3 *- Statistical distribution of BOD in some French and Moroccan rivers (for sources, see tab. 4.1). The horizontal line represents the median value and the yellow boxes represent the 25th and 75th percentiles, respectively. The vertical lines outside the boxes are the maximum and minimum values, respectively (not available for the Moroccan rivers).*

Going further to the south, the situation can be more extreme. The Martil River in Morocco, a typical "oueds" (a coastal river that is dry during certain periods of the year), has a median BOD value of about 9 mg/l, which is among the highest values of the rivers in table 4.1. But the variability of the values is even more striking: about one quarter of the values are greater than 28 mg/l (fig. 4.3). In the Moulouya River, which is a relatively large Moroccan river that flows permanently, BOD values are much lower. Specific wastewater inputs to this river may be less important, but part of the better water quality is certainly also related to the fact that the auto-purification capacity of this river is greater. However, even if the median value of the Moulouya River is comparable to most of the coastal rivers in France, it is indicated that the variability of the values is still somewhat greater than for the French rivers (fig. 4.3).

4.4 – BOD Trends

The above-described data mainly reflect the organic pollution in the Mediterranean rivers about 10-15 years ago. In the meantime, the situation has improved for many rivers. Organic pollution in rivers depends upon the socio-economic and technological evolution of the societies in the river basins, which are highly dynamic. It is mainly from the 1940s onwards that increased industrial and agricultural production coupled with more of the population being connected to sewerage meant that the discharge of organic waste into surface water increased in most European countries (EEA, 1999). Over the past 15-30 years however, biological treatment of wastewater has increased, and the organic loading has consequently decreased in many parts of Europe. The result is that many rivers that suffered from organic pollution are now well oxygenated.

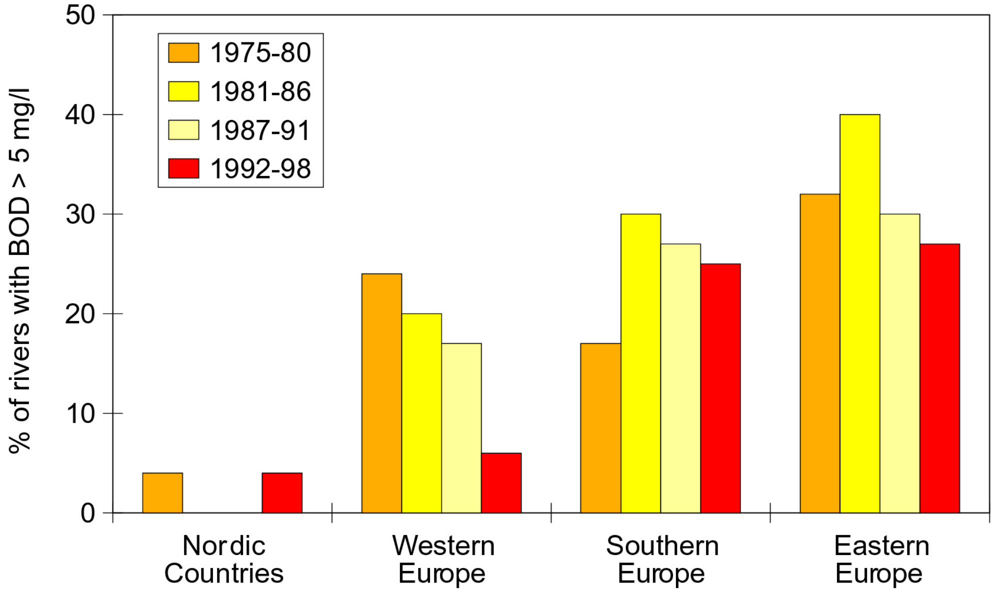

Fig. 4.4 *- Percentage of heavily polluted rivers in Europe. Figure from EEA, 1999.*

Particularly in the most polluted rivers, the concentration of organic matter in European rivers has fallen over the last decades due to improvements in the treatment of domestic sewage and industrial wastewater. But purification techniques are expensive, and this mainly concerns the richer countries. According to EEA (1999), there has been a marked and continuous decrease in the number of heavily polluted rivers in western Europe from 24% in the late 1970s to 6% in the mid-1990s (fig. 4.4). But in southern Europe, where many of the Mediterranean rivers are situated, the decrease only started in the 1980s and is much less significant (from about 30 to 25% - fig. 4.4). No information was available about the north African rivers that are discharging to the Mediterranean Sea, but it can be expected that, if there was any improvement, it was not as important as in the western European rivers.

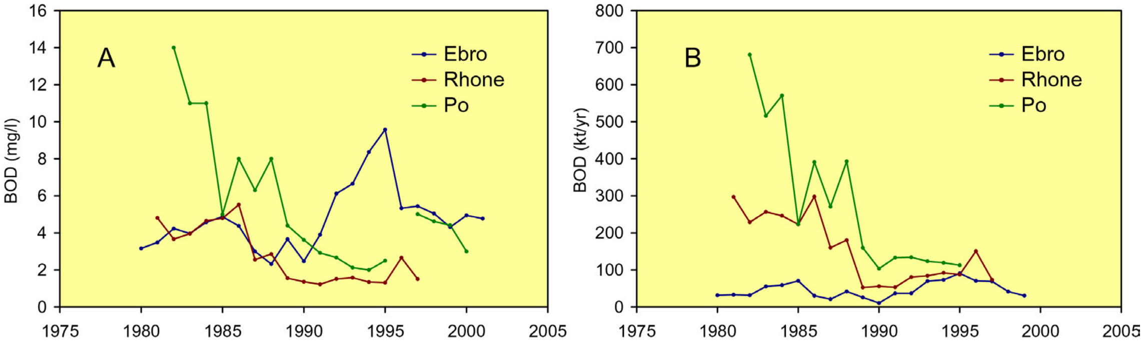

***Fig. 4.5** - Evolution of BOD concentrations (A) and loads (B) in the Ebro (at Tortosa), Po (at Pontelagoscuro) and Rhone (at Arles) rivers. Data sources: Kristensen, 1997 for the Po River (except for the 1997 to 2001 data which have been supplied by the Po River Authority); "Confederación Hidrográfica del Ebro" (http://www.oph.chebro.es/#) for the Ebro, River and the French monitoring Agency "Agence de l'Eau Rhône - Méditerranée - Corse (http://www.rdbrmc.com/) for the Rhone River. For the Rhone and Ebro rivers, discharge weighted mean concentrations could be calculated, whereas for the Po Rivers only arithmetic means were available.*

The evolution of the BOD concentrations and loads in the Rhone, Po and Ebro rivers are good examples to illustrate the general trend during the last 20 years (fig 4.5). At the beginning of the 1980s, the Po was heavily polluted, with average BOD concentrations far above 10 mg/l. Since then, the values decreased starkly, and they are nowadays below the 5 mg/l limit (fig 4.5a). Also in the Rhone River, BOD concentrations decreased considerably during the same period, but the values were already much lower at the beginning of the 1980s compared to the Po River. Nowadays, the Rhone seems to be free of organic pollution. The evolution in the Ebro River, however, is opposite to these trends. In this river, the BOD levels rather increased during the last decades. Apparently, wastewater treatment was not improved in this basin, or any improvement was compensated by a greater number of pollution sources.

Comparing average concentrations alone does, of course, not allow estimating the exact changes of the wastewater inputs because of the variations in water discharge (see chapter II) in these rivers. When looking at the BOD loads (fig 4.5a), one can notice that from the beginning of the 1980s to the beginning of the 1990s, the BOD loads depict a three- to fivefold reduction in the BOD inputs in the Rhone and Po rivers respectively. In the Ebro, the loads are less variable but rather tend to increase towards recent years. It has to be noted that around 1995, the BOD load in the Ebro was about the same as in the Rhone, although the water discharge of the Rhone is on average 5-6 times greater than the water discharge of the Ebro.

4.5 – Bacteriological pollution

In many cases, organic pollution in rivers is also accompanied by bacteriological pollution, since wastewater inputs from households and agriculture (especially with animal farming) often contain great numbers of bacteria and viruses that are pathogenic for humans. Also the organisms living in the aquatic ecosystems may suffer from these pathogens. Harmful pathogens, however, are generally difficult to detect and to monitor directly in freshwaters. Therefore, counts of indicator bacteria are normally used to assess microbiological water quality. These bacteria are harmless themselves, but their presence in high numbers indicates that the water may be contaminated. The most widely used indicator bacteria are of the total coliform, faecal coliform, enterococci and faecal streptococci groups, and *Escherichia coli* (US Geological Survey, 1997 to present - see tab. 4.2).

***Table 4.2** - Ranges of faecal indicator bacteria typically found in surface water and contaminated surface water (from US Geological Survey, 1997 to present)*

Bacterial group	Surface water (n/100ml)	Contaminated surface water (n/100ml)
Total coliforms	< 1 to 80 000	1 200 to > 4 000 000
Faecal coliforms	< 1 to 5 000	200 to > 2 000 000
Escherichia coli	< 1 to 576	126 to > 2 000 000
Faecal streptococcus	< 1 to 1 000	400 to > 1 000 000

For this study, we only disposed data on bacterial counts for 13 Mediterranean rivers (tab. 4.3 and fig. 4.6a). Most of them are Greek and Italian rivers, and the observation period mainly corresponds to the second half of the 1980s. According to these data, the most polluted rivers are the Po, Tiber and Ebro rivers, which is principally in agreement with the BOD and COD data in table 4.1. Lowest bacteria counts were found in the Rhone and Akheloos rivers. Ranking of the rivers naturally depends to some extent on the choice of the indicator bacteria. One may also mention here that a precise evaluation of the averages of bacteria numbers may be more difficult than for other constituents in river water because of the great variability of the values. A determination of representative averages should also take into account the hydrological and climatic conditions under which the samples have been takes, allowing, for example, the calculation of discharge-weighted averages. This information was not available to this study. Nevertheless, the data is interesting because it is somewhat complementary to the data in table 4.1. Especially for certain Greek rivers, bacterial counts were available, whereas BOD and COD values are missing (such as the Akheloos, Aliakmon, Axios and Strymon rivers). Except for the Strymon River, which has a rather high degree of pollution, this is indicating that the pollution level of the other rivers is rather moderate.

Table 4.3 - Bacteriological water quality in some Mediterranean rivers (all data from Kristensen (1997), except for the Rhone River where the data are from the "Agence de l'Eau Rhône - Méditerranée - Corse (http://www.rdbrmc.com/).

Rivers	Country	Coli-faecal (n/100ml)			Coli-total (n/100ml)			Strepto-faecal (n/100ml)			period	sample nb
		mean	min	max	mean	min	max	mean	min	max		
RHONE	Fr				2100	30	11700	515	1	6000	88-92	52
AKHELOOS	Gr	133	0	4600	301	0	4600	32	0	266	84-92	71
ALIAKMON	Gr	3520	0	240000	12423	6	1000000	765	0	24500	82-92	103-104
AXIOS	Gr	5320	240	46000	10740	450	46000	1892	0	11000	83-89	51
NESTOS	Gr	1696	0	11000	3106	23	24000	905	0	8000	82-92	55
PINIOS	Gr	1159	0	11000	2677	0	37000	78	0	700	82-91	72-91
STRYMON	Gr	14830	43	1000000	20395	110	1000000	2883	0	30000	82-92	116-117
ADIGE	It	2335	0	36300	14007	200	90200	409	0	4200	87-92	74
ARNO	It	2752	50	9180	7355	200	24000	393	20	2300	88-92	42
METAURO	It	5549	10	36000	6146	30	100000	783	0	9180	84-92	55-58
PO	It	26636	1000	330000	57203	1000	1000000	10133	700	302000	82-92	113
TEVERE	It	188454	4300	2000000	284024	7500	4000000				89-91	17-18
EBRO	Sp	11790	7	456000	106756	38	810000	138	0	2500	87-92	69-75

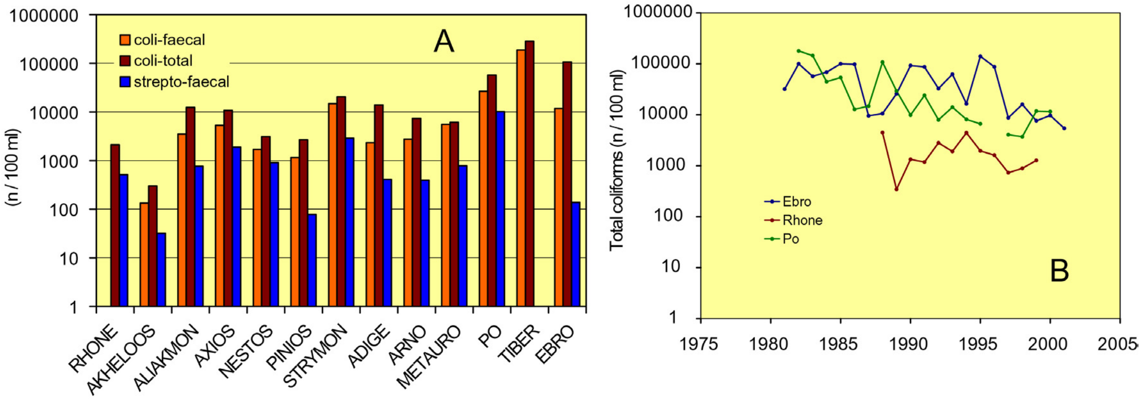

Fig. 4.6 - (A) Averages of faecal indicator bacteria in some Mediterranean rivers (same sources as tab. 4.3) and (B) evolution of total coliforms in the Rhone, Po and Ebro rivers during recent years (same sources than in fig. 4.5).

For the three larger river basins of the Rhone, Po and Ebro rivers, we also found more recent data in order to evaluate whether there are trends in the evolution of the bacteriological water quality (fig. 4.6b). These trends are in good agreement with the evolution of the BOD levels in these rivers (fig. 4.5a,b). For the Po River, there is an ongoing improvement of the water quality from the beginning of the 1980s, whereas the water quality of the Ebro River remains bad (although a slight improvement may be visible). The best water quality is found in the Rhone River.

Chapter V – Nutrients

5.1 - Introduction

A nutrient is a chemical compound (carbon, nitrogen, phosphorous, etc.), which can be used directly by living cells for nutrition or can be assimilated without prior digestion (Encyclopaedia Universalis). Strictly speaking, the word 'nutrients' therefore refers to a large range of substances with variable concentration levels, chemical behaviours and effects on the environment. Nutrients are essential for maintaining primary production in aquatic ecosystems and are hence no pollutants per se. An excess of nutrients, however, may allow primary producers to develop in too great abundance in order to be supported by the ecosystem, a process that is commonly designed as 'eutrophication'. Excessive algae growth may then be followed by severe oxygen depletion when the algae die and their organic matter is mineralised. This may be harmful for the other animals living in the aquatic system. Moreover, as a secondary effect, low oxygen levels may also enhance the availability and mobility of other pollutants, such as heavy metals.

This chapter deals with only those nutrients that are important in terms of their nutritive value for plants and nuisance level. They are in practice phosphorous and nitrogen compounds (also called 'macro-nutrients'). Plant growth in the aquatic environment results from photosythesis, which can be summarised by two general chemical equations (Stumm and Morgan, 1981), depending on the source of nitrogen being used:

$$106\ CO_2 + 64\ H_2O + 16\ NH_3 + H_3PO_4 \text{ --> } C_{106}H_{179}O_{68}N_{16}P + 106\ O_2 \quad (i)$$

$$106\ CO_2 + 64\ H_2O + 16\ HNO_3 + H_3PO_4 \text{ --> } C_{106}H_{179}O_{68}N_{16}P + 138\ O_2 \quad (ii)$$

According to these equations, the proportions of the major components of phytoplanktonic species can be considered as quite constant, following the molar C/N/P ratios of 106/ 16/ 1. This ratio is often named the 'Redfield ratio', after the author who established it through observations of marine phytoplankton around 1930 (Redfield, 1963). In the different ecosystems, of course, variations around the average ratio values can be found depending on the species being present and on the physiological state of the cells.

Either the concentration of C, N, or P can limit primary production, even if the other elements are present at high levels. In open systems that are in contact with the atmosphere, carbon is never a limiting factor since it can be supplied by atmospheric CO_2. Also nitrogen can be supplied by atmospheric N_2 via the so-called process of nitrogen fixation, although this requires the presence of special bacteria species, which are not always present in the aquatic systems. Phosphorous is the only element where no gaseous compound is involved in the cycling of this nutrient. Consequently, it is often the availability of this element that limits primary production, and elevated phosphorous levels are in most of the cases the fundamental cause of eutrophication (Crouzet et al., 1999).

Dissolved silica is another element that is commonly included in the group of macronutrients. Silica is not involved in the synthesis of organic matter, but it is an important element for the constitution of hard parts of diatoms. When diatoms are the dominant species among the phytoplankton communities, as this is often the case in the Mediterranean Sea (Bethoux et al., 2002), the availability of silica also may limit primary production. Natural riverine silica fluxes can be strongly impacted by silica retention in reservoirs, as it has been shown recently for the Danube River (Humborg et al., 1997). Despite this, we did not include silica in our study because the availability on data on this parameter in Mediterranean rivers is too scarce.

5.2 – Forms and levels of N and P in rivers

5.2.1 – Global fluxes

Carbon, nitrogen and phosphorous occur in rivers both in the dissolved and particulate forms, and both in the form of inorganic and organic species. From a global point of view (tab. 5.1), carbon is mainly transported in the dissolved forms, especially as inorganic carbon (bicarbonate ions). For nitrogen, particulate organic nitrogen (PON) is the dominant form, although dissolved inorganic nitrogen (DIN) becomes more and more important due to the increasing anthropogenic contribution (see below). Rocks do not contain N-bearing minerals and particulate inorganic nitrogen is normally absent in rivers, even if some DIN may be absorbed on particles (mainly ammonia) and hence be transported in the particulate form.

Table 5.1 *- Global fluxes of carbon, nitrogen and phosphorous to the worlds oceans*

Carbon (TgC/yr)		Nitrogen (TgN/yr)		Phosphorous (TgP/yr)	
DOC	200	DON	10	DOP	?
DIC	380	DIN	12	DIP	2
POC	180	PON	21	POP	8
PIC	170	PIN	-	PIP	12
dissolved	580		22		2
particulate	350		21		20

Explanations: D = dissolved, P = particulate; I = inorganic, O = organic; C = carbon, N = nitrogen, P = phosphorous. Data compiled from Foellmi (1996), Ludwig et al. (1996), and Meybeck (1982).

The particulate phase is by far the dominant transport form for phosphorous in rivers, especially as particulate inorganic phosphorous (PIP). But it is probably also here where it is the most difficult to distinguish between the transport in the dissolved and particulate forms. Unlike nitrogen compounds, phosphorous species may be strongly bound to suspended or settled material. The P content of rivers can thus be governed by a ‘spiral pattern’ (Amoros and Petts, 1993) involving the sediment phase to which phosphorous species are bound and released from. Finally, one has to mention that the N and P fluxes related to the transport of dissolved organic matter (DOM) are the most difficult to assess. In the particulate organic matter, the element ratios are rather constant; at least as far as the C/N ratios are concerned (Ittekkot and Zhang, 1989). But studies on the element ratios in DOM are rare and difficult to generalise. We did not find any global estimate for the dissolved organic phosphorous (DOP) transport in rivers.

5.2.2 - Monitoring of N and P species

The above-given values are based on global flux considerations that do not necessarily take into account the spatial variability on Earth, as well as the dynamic evolution of these fluxes during recent years. The budgets for the particulate fluxes are dominated by a few high turbid rivers (such as the Asian rivers draining the Himalayan region), and they were strongly affected during recent years by the sediment retention in reservoirs (see chapter III), which also should have reduced the riverine fluxes of particulate nutrients.

Table 5.2 *- Relative importance of the different nitrogen and phosphorous species in the Po, Rhone and Ebro rivers.*

River	Nitrogen						Phosphorus				source
	TN mg/l	N-NO_3 %	N-NO_2 %	N-NH_4 %	DON %	PN %	TP mg/l	P-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)

Sources: (1) Tartari et al., 1991; (2) Pont, 1996; (3) Munoz and Prat, 1989.

When looking at the proportions of specific forms of nutrients in individual rivers, the dissolved forms are therefore often more important as it might be expected from the global budgets. In the case of nitrogen, nitrate is normally the dominant form (tab. 5.2). The other DIN species (NO_2^- and NH_4^+) are only abundant when there the rivers suffer from organic pollution, reducing the oxygen levels and allowing hence the reduced forms to be stable. This makes that the monitoring of nitrate is normally sufficient to evaluate the eutrophication potential in rivers related to nitrogen enrichment.

In the case of phosphorous, however, the particulate forms cannot be neglected (tab. 5.2) compared to the dissolved forms (mainly phosphate). National monitoring agencies also determine the total phosphorous (TP = sum of all dissolved and particulate P species) content in rivers, although it is not known whether this phosphorous is really biologically available or not. Another problem is that TP concentrations can be strongly coupled to the concentrations of total suspended solids (fig. 5.1), making it difficult to monitor this parameter accurately. As mentioned in chapter III, the sampling frequency of most monitoring programs is normally too scarce to determine reliable average sediment concentrations, which also affects the concentrations of TP. This has to be kept in mind when considering the temporal and spatial variability of average TP levels in rivers. Phosphate levels are less variable and, even if phosphate is not necessarily the dominant P form, average values might sometimes be more suitable for trends analyses in order to assess the evolution of nutrient pollution in rivers.

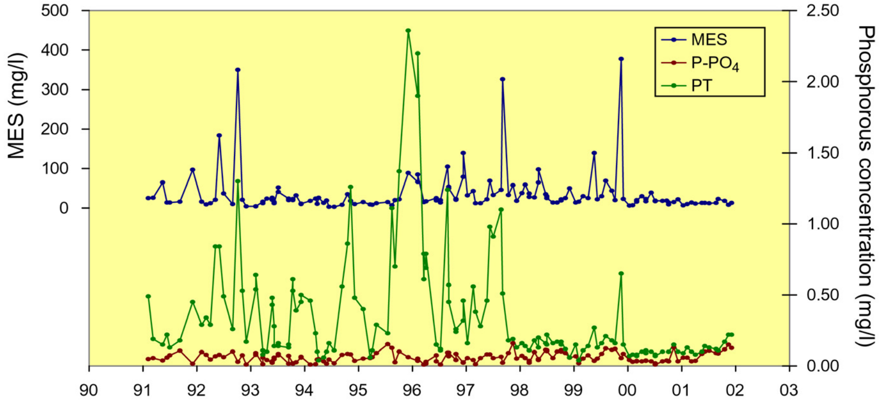

Fig. 5.1 *- Evolution of MES, P-PO4 and TP in the Aude River at Moussan in southern France. The data are from the French monitoring Agency "Agence de l'Eau Rhône - Méditerranée - Corse (http://www.rdbrmc.com/) and represent monthly sampling.*

5.2.3 – Sources of pollution

Best estimates for the natural levels in nitrogen and phosphorous species in rivers are given in table 5.3a, in comparison with the commonly applied limits for polluted surface waters in the EEC countries. The natural levels were derived from data presently monitored in quasi-pristine areas, and it is not clear whether they really can be applied to the Mediterranean rivers. The latter have been impacted by man for centuries, long before any measurement could be performed, whereas pristine areas are normally situated in mountains or in northern regions, and do not necessarily represent the natural values of lowlands or southern river systems.

In almost all of the densely populated regions of the world, pollution became nowadays the principal source of N and P nutrients in rivers. The actual concentration levels may easily be one, sometimes two orders of magnitude higher than the natural levels. But even if elevated nitrogen concentrations are normally also accompanied by elevated phosphorous concentrations, both nutrients do not have the same origins.

For the beginning of the 1990s, Crouzet et al. (1999) estimated that in the more densely populated areas of Europe, about 50-75% of the dissolved phosphorous load to inland waters is derived from point sources, while agriculture generally accounts for 20-40% (see also tab. 5.3b). Municipal sewage discharge makes the bulk of the total point source discharges. The extent to which this is discharged into surface waters naturally depends on the wastewater treatment facilities available. Traditional wastewater treatment plants were designed primarily for the reduction of organic matter, and the nutrient loads were largely unaffected. The treatment of municipal wastewater in Europe has significantly improved during the past 10 to 15 years, especially in southern Europe. A larger percentage of the population has been connected to treatment plants and the treatment level has changed. In eastern and southern Europe, there has been a pronounced change from primary (mechanical) to secondary (biological) treatment. The introduction of tertiary treatment, most often with phosphorous removal, has been a predominant trend especially in western Europe and Nordic countries (Crouzet et al., 1999).

***Table 5.3a** - Natural levels and pollution limits for nutrients in river water*

Compound	Natural levels	Standard for water quality	
		Guide level	Maximum admissible concentration
$N\text{-}NO_3$	0.100 mg N/l	5.65 mg N/l	11.29 mg N/l
$N\text{-}NH_4$	0.015 mg N/l		
$P\text{-}PO_4$	0.010 mg P/l		
TP	0.017 mg P/l	0.18 mg P/l	2.18 mg P/l

Sources: Meybeck (1982; 1986) for the natural levels, and Crouzet et al. (1999) for the water quality standards.

Nitrogen pollution is usually dominated by diffuse sources, in particular agriculture (tab. 5.3b). In those catchments draining the central and western part of Europe, about 45-90% of the nitrogen load to inland waters is related to agriculture (Crouzet et al., 1999). The next important nitrogen sources are point sources, predominantly municipal sewage treatment plants. The deposition of nitrogen oxides (NOx) to land and surface water may also contribute to increased N loads and eutrophication. The main source of NOx is the transport sector. This sector increased considerably during recent years, but the increasing emissions arising from car transport has to some extent been reduced by the introduction of catalysts for petrol cars.

***Table 5.3b** - Relative importance of the different nitrogen and phosphorous sources in the Po River in 1989 (from Crouzet et al., 1999)*

Compound	Point Source	Agriculture	Natural
P	67.0%	32.0%	1.0%
N	42.9%	54.0%	3.1%

5.3 – N and P levels in Mediterranean rivers

The available data on the average nutrient concentrations in the Mediterranean rivers are presented in table 5.4. Since the nutrient levels are variable over time (see below), the reference periods corresponding to the average values are given whenever this information was available. For many rivers, several estimates are available. They are, in most of the cases, not too different from each other. In some cases, however, some ‘outliers’ might exist, which may be due to badly verified data sources or to calculation errors.

Table 5.4 *- Average nutrient concentrations in various Mediterranean rivers (for source indexes, see reference list)*

Rivers	Country	$N\text{-}NO_3$ - mg/L	period	source	$N\text{-}NO_2$ - mg/L	period	source	$N\text{-}NH_4$ mg/L	period	source	N k mg/L	period	source	$P\text{-}PO_4$ mg/L	period	source	Tot P mg/L	period	source
ADIGE	Italy	**1.248**	87-92	*97.007*				**0.111**	84-92	*97.007*				**0.033**	89.000	*97.007*	**0.113**	87-92	*97.007*
		0.940	70-80	*85.200*				**0.130**	70-80	*85.200*				**0.050**	70-80	*85.200*	**0.165**		*95.017*
AKHELOOS	Greece	**0.350**	90	*98.002*	**0.010**	90	*98.002*	**0.020**	90	*98.002*							**0.020**	90	*98.002*
		0.169	82-92	*97.007*				**0.035**	82-92	*97.007*							**0.015**	82-92	*97.007*
		0.600	83-84	*97.014*										**0.020**	83-84	*97.014*			
ALIAKMON	Greece	**2.350**	94/95	*98.001*	**0.060**	94/95	*98.001*	**0.110**	94/95	*98.001*							**0.140**	94/95	*98.001*
		0.250	90	*98.002*	**0.010**	90	*98.002*	**0.010**	90	*98.002*							**0.030**	90	*98.002*
		0.395	82-92	*97.007*				**0.050**	82-92	*97.007*							**0.017**	82-92	*97.007*
		0.770	83-84	*97.014*										**0.100**	83-84	*97.014*			
ARGENS	France	**0.740**	85-96	*97.005*	**0.020**	85-96	*97.005*	**0.090**	85-96	*97.005*	**0.500**	85-96	*97.005*	**0.110**	85-96	*97.005*	**0.220**	85-96	*97.005*
ARNO	Italy	**3.620**	90-92	*97.007*				**1.347**	89-92	*97.007*				**0.500**		*85.200*	**0.406**	89-92	*97.007*
		1.000	77-83	*91.081*				**1.190**	77-83	*91.081*							**0.860**	77-83	*91.081*
AUDE	France	**1.420**	85-96	*97.005*	**0.030**	85-96	*97.005*	**0.090**	85-96	*97.005*	**1.200**	85-96	*97.005*	**0.090**	85-96	*97.005*	**0.490**	85-96	*97.005*
AXIOS	Greece	**2.590**	94/95	*98.001*	**0.020**	94/95	*98.001*	**0.150**	94/95	*98.001*							**0.880**	94/95	*98.001*
		1.900	90	*98.002*	**0.320**	90	*98.002*	**0.050**	90	*98.002*							**1.000**	90	*98.002*
		1.584	82-92	*97.007*				**0.066**	82-92	*97.007*				**0.480**		*97.015*	**0.574**	82-92	*97.007*
		1.180	83-84	*97.014*										**0.270**		*92.064*	**0.480**	83-84	*97.014*
BESOS	Spain	**1.900**	94-95	*97.008*	**0.300**	94-95	*97.008*	**31.000**	94-95	*97.008*							**12.700**	90-92	*97.010*
BUYUK MENDERES	Turkey	**1.440**		*97.015*										**0.550**		*97.015*			
CEYHAN	Turkey																**8.680**		*97.015*
EBRO	Spain	**2.323**	86-92	*97.007*				**0.167**	86-92	*97.007*				**0.115**	86-87	*90.180*	**0.243**	86-92	*97.007*
		1.500	79-82	*95.001*				**0.100**	79-82	*95.001*				**0.029**	79-82	*95.001*			
EVROS	Greece	**1.900**	83-84	*97.014*										**0.280**	83-84	*97.014*			
		1.400	<84	*87.192*				**0.050**	<84	*87.192*				**0.360**	<84	*87.192*			
		1.640		*97.015*															
FLUVIA	Spain							**0.054**	90-92	*97.010*							**0.350**	90-92	*97.010*
GEDIZ	Turkey	**1.650**	<84	*87.192*				**0.050**	<84	*87.192*				**0.190**	<84	*87.192*			
GOKSU	Turkey																**8.870**		*97.015*
HERAULT	France	**0.610**	85-96	*97.005*	**0.012**	85-96	*97.005*	**0.060**	85-96	*97.005*				**0.045**	85-96	*97.005*	**0.220**	85-96	*97.005*
KISHON	Israel																**20.000**		*97.015*
KRKA	Croatia	**0.526**	90	*97.007*	**0.001**		*97.011*	**0.093**	90	*97.007*				**0.046**	90	*97.007*			
		0.450	70-90	*97.011*				**0.031**	70-90	*97.011*				**0.029**	70-90	*97.011*			

Table 5.4 *- (continued)*

Rivers	Country	N-NO$_3$ - mg/L	period	source	N-NO$_2$ - mg/L	period	source	N-NH$_4$ mg/L	period	source	N k mg/L	period	source	P-PO$_4$ mg/L	period	source	Tot P mg/L	period	source
LLOBREGAT	Spain	**1.900**	94-95	*97.008*	**0.500**	94-95	*97.008*	**3.200**	94-95	*97.008*				**1.200**	94-95	*97.008*	**1.530**	90-92	*97.010*
								4.100	90-92	*97.010*							**1.250**		*84.223*
METAURO	Italy	**1.366**	84-92	*97.007*										**0.005**	84-90	*97.007*	**0.119**	87-92	*97.007*
NERETVA	Croatia	**0.269**	78-90	*97.007*				**0.029**	80-90	*97.007*							**0.050**	78-90	*97.007*
		0.489		*97.011*				**0.002**		*97.011*							**0.023**		*97.011*
NESTOS	Greece	**0.780**	90	*98.002*	**0.010**	90	*98.002*	**0.040**	90	*98.002*							**0.120**	90	*98.002*
		1.239	82-92	*97.007*				**0.094**	92-94	*94.064*							**0.127**	82-92	*97.007*
		3.520	83-84	*97.014*				**0.071**	82-92	*97.007*							**0.130**	83-84	*97.014*
		0.810		*97.015*															
NILE	Egypt	**3.000**	93	*99.002*															
ORB	France	**0.670**	85-96	*97.005*	**0.045**	85-96	*97.005*	**0.440**	85-96	*97.005*	**0.900**	85-96	*97.005*	**0.140**	85-96	*97.005*	**0.450**	85-96	*97.005*
PINIOS	Greece	**1.890**	94/95	*98.001*	**0.010**	94/95	*98.001*	**0.090**	94/95	*98.001*							**0.140**	94/95	*98.001*
		3.000	90	*98.002*	**0.020**	90	*98.002*	**0.050**	90	*98.002*							**0.070**	90	*98.002*
		2.323	86-92	*97.007*				**0.167**	86-92	*97.007*							**0.243**	86-92	*97.007*
		1.200		*97.015*													**0.260**		*97.015*
PO	Italy	**2.192**	82-92	*97.007*				**0.261**	82-92	*97.007*							**0.239**	82-92	*97.007*
		2.030		*91.094*				**0.210**		*91.094*				**0.084**		*91.094*	**0.230**		*91.081*
		1.430		*85.200*				**0.270**		*85.200*				**0.075**		*91.081*			
RHONE	France	**1.320**	94-95	*96.032*	**0.019**	94-95	*96.032*	**0.091**	94-95	*96.032*	**0.230**	94-95	*96.032*	**0.044**	94-95	*96.032*	**0.124**	94-95	*96.032*
		1.480	85-96	*97.005*	**0.033**	85-96	*97.005*	**0.124**	85-96	*97.005*	**0.800**	85-96	*97.005*	**0.101**	85-96	*97.005*	**0.140**	85-96	*97.005*
								0.450	79-80	*83.247*				**0.128**	84+89+90	*93.022*			
SEMANI	Turkey	**0.240**	90	*97.007*													**0.002**	90	*97.007*
SEYHAN	Turkey	**0.590**	<84	*87.192*				**0.310**	<84	*87.192*	**0.270**	<84	*87.192*	**0.010**	<84	*87.192*			
SHKUMBINI	Albania	**0.730**	90	*97.007*													**0.010**	90	*97.007*
STRYMON	Greece	**1.100**	90	*98.002*	**0.010**	90	*98.002*	**0.030**	90	*98.002*							**0.110**	90	*98.002*
		1.236	82-92	*97.007*				**0.053**	82-92	*97.007*				**0.110**		*97.015*	**0.125**	82-92	*97.007*
		0.960	83-84	*97.014*													**1.380**	83-84	*97.014*
		0.960		*97.015*															
TAVIGNANO	France	**0.340**	85-96	*97.005*	**0.045**	85-96	*97.005*	**0.003**	85-96	*97.005*				**0.005**	85-96	*97.005*			
TER	Spain							**1.200**	90-92	*97.010*							**2.150**	90-92	*97.010*
								5.000		*95.058*							**0.800**		*95.058*
TET	France	**1.800**	85-96	*97.005*	**0.180**	85-96	*97.005*	**1.500**	85-96	*97.005*	**2.700**	85-96	*97.005*	**0.470**	85-96	*97.005*	**0.800**	85-96	*97.005*
TIBER	Italy	**1.370**	79-83	*91.081*				**1.038**	83-91	*97.007*							**0.355**	83-91	*97.007*
		0.024	91	*97.007*				**1.420**	79-83	*91.081*				**0.260**	79-83	*91.081*	**0.440**	79-83	*91.081*
																	0.455		*95.017*
VAR	France	**0.180**	85-96	*97.005*	**0.003**	85-96	*97.005*	**0.031**	85-96	*97.005*	**1.500**	85-96	*97.005*	**0.006**	85-96	*97.005*	**0.130**	85-96	*97.005*

5.3.1 – Nitrate

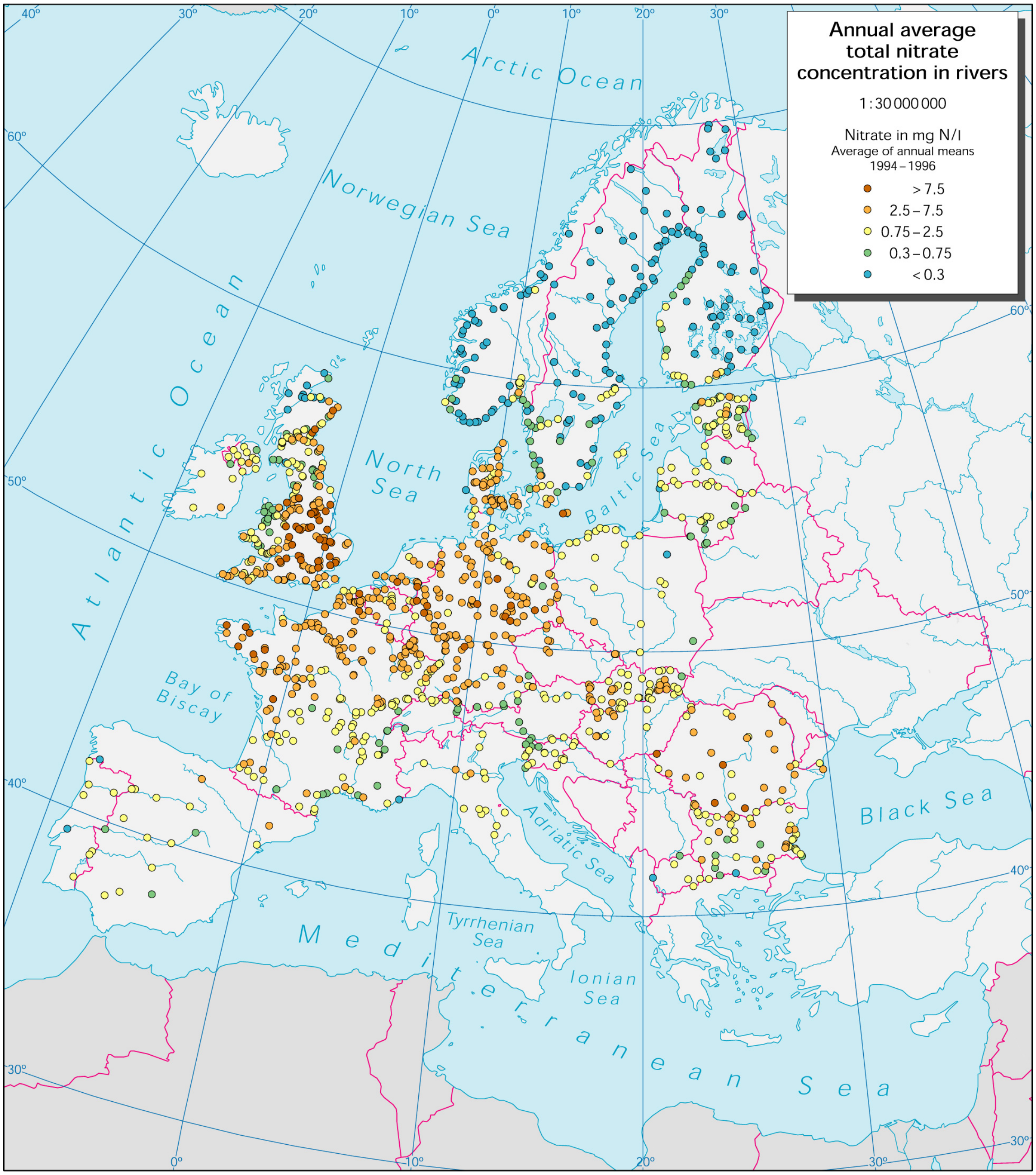

Fig. 5.2 - *Nitrate in European rivers from 1992 to 1996 (figure from Crouzet et al., 1999)*

For nitrate, the data coverage is best. More than 30 rivers are documented with average values. The median nitrate concentration is about 1.24 mg N/l, with a rather low variability of the values. This is indicating that most of the Mediterranean rivers are affected by nitrate pollution. The pollution level is, however, low compared to other European rivers (fig. 5.2). Apart from the rivers in the Nordic countries, where many of the rivers are still in a pristine state, the highest concentrations up to >20 mg N/l were found in the northern part of western Europe, reflecting the intensive agriculture in these regions. This picture of decreasing concentrations towards the south is in good agreement with the general practice of nutrient application to agricultural land (inorganic fertiliser and manure), varying in Europe from about 180 kg N/ha in the Netherlands in 1991 to 30-70 kg N/ha in southern Europe (Crouzet et al., 1999).

Elevated concentrations among the rivers listed in table 5.4 are found in the intensely cultivated river basins of Italy, Spain, and/or Greece, such as the Arno, Po, Ebro and/ or Pinios rivers. Also the Nile River has one of the highest average nitrate concentrations, although this value has been derived from only a few published values and it is not clear whether this value really is representative for this river. If the organic pollution level is too elevated, however, the bulk of the inorganic nitrogen is transported in the reduced form (NO_2^- and NH_4^+), which is hence not necessarily leading to elevated nitrate concentrations. This is the case, for example, for the Besos River, which receives the wastewaters of Barcelona in Spain. The lowest nitrate concentrations of clearly less than 1 mg N/l are typical for rivers where agriculture may be less intense in the catchments, and/ or accompanied by crops that do not require much fertiliser (such as the Var, Tavignano and Herault rivers in France). Also the rivers of Croatia seem to have rather low nitrate values (e.g. the Krka and Neretva rivers), but in these cases this may at least partly also be a dilution effect. Nitrogen inputs may be more diluted due to the often-high drainage intensities in these rivers (see chapter II).

5.3.2 – Phosphorous

The average phosphorous levels in the Mediterranean rivers are generally in agreement with the nitrate levels, even if the data coverage is less important. The median phosphate and total phosphorous concentrations of all rivers are 0.10 and 0.24 mg P/l, respectively. Also here, the values indicate a rather moderate pollution level compared to the rivers in the northern part of western Europe (fig. 5.3). In the case of phosphorous, the spatial variability of the values can be greater than in the case of nitrogen, because of the stronger dependence of phosphorous loads to point source pollution. As a consequence, the differences between the upstream and downstream stations within an individual river basin is often more important than for nitrate, and the regional patterns are less clear (fig. 5.3). Also the stations in the countries of southern Europe can depict high pollution levels, such as along the Mediterranean coast in southern France.

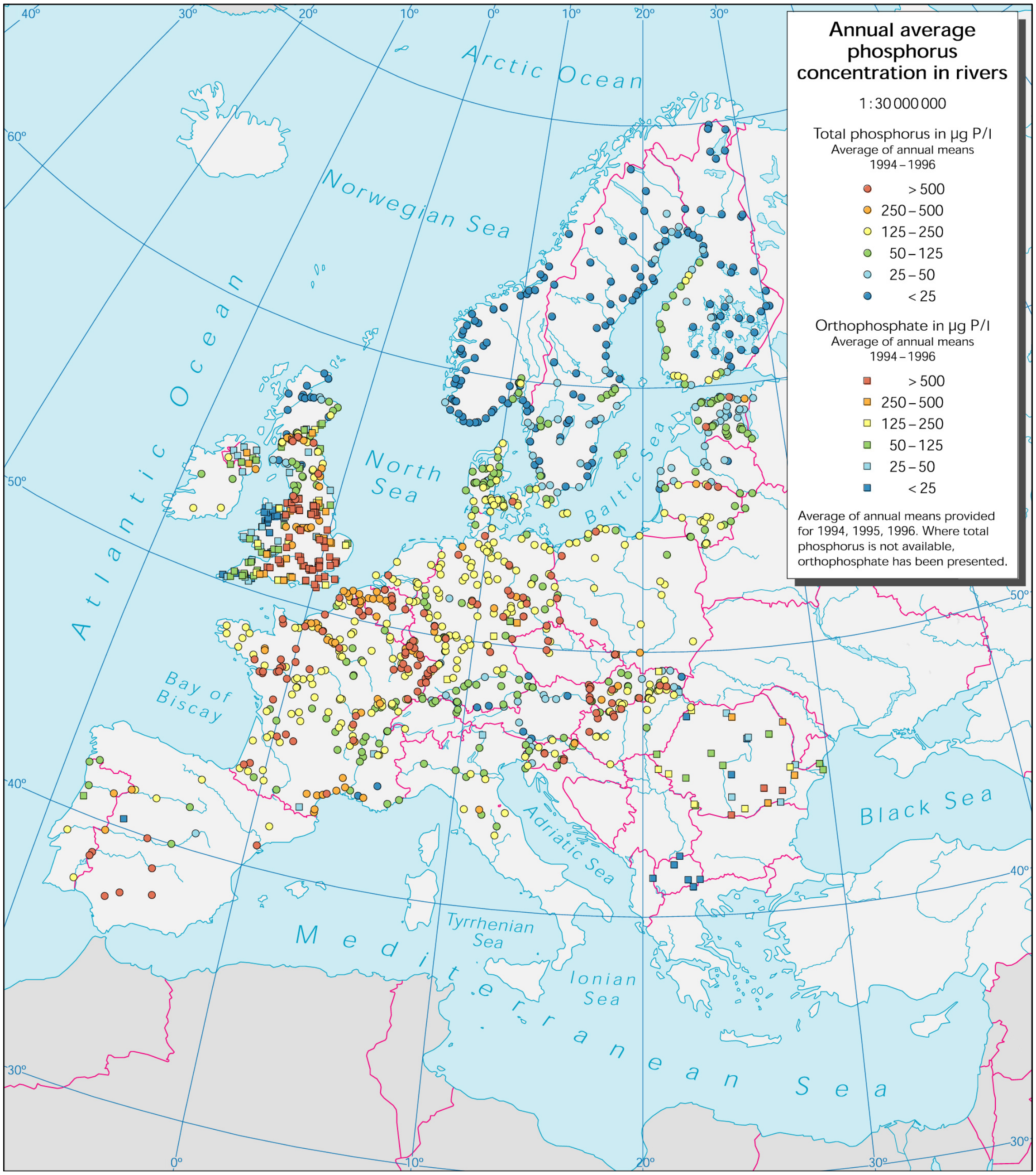

***Fig. 5.3 -** Phosphorous in European rivers from 1994 to 1996 (figure from Crouzet et al., 1999)*

Ranking the Mediterranean rivers in table 5.4 according to their average phosphorous concentrations does therefore not exactly follow the ranking of nitrate pollution. Highest P values are typical for the rivers suffering from organic pollution due to urban wastewater inputs (see also chapter V), such as the Besos and Llobregat in Spain, the Axios in Greece, the Tet in France and/ or the Arno in Italy. Lowest phosphorous concentrations are also found in the rivers with low nitrate concentrations (e.g. the Var or the Neretva rivers), indicating that these rivers are probably the closest to a pristine state.

5.4 – Trends

The average values in table 5.4 stretch over the period of about the last 30 years, with most of the values representing the 1980s and the beginning of the 1990s. It can be expected that the nutrient levels did not remain stable over these periods, as it is indicated by the variability of the values when different estimates were available for individual rivers. However, since the values often refer to different time slices, and may have been determined by different methods, they cannot directly be used for the evaluation of trends. Knowing these trends is nevertheless crucial for an evaluation of the impact of riverine nutrient levels on the Mediterranean ecosystems. Primary and secondary producers in the oligotrophic waters of the Mediterranean Sea adapted to low nutrient levels, and abrupt changes in the riverine nutrient loads may considerably affect the biological systems, even if the average concentrations are rather moderate compared to other densely populated regions of the world.

5.4.1 – Large river basins

Monitoring programs for large river systems are generally better developed than for small rivers, and water quality data are more easily accessible. Another advantage is that large river basins integrate the variety of human activities at regional scales, making them more representative than smaller basins. For these reasons, we focus in our trend evaluation first of all at the evolution of the nutrient concentrations in the Rhone, Po and Ebro rivers. We found for all three rivers data on the annual nutrient concentrations for about the last 30 years, allowing the establishment of a detailed picture of the evolution during this time (figs. 5.4a and 5.5a). Moreover, together with the discharge data for these rivers of chapter II, also the evolution of the annual nutrient loads can be examined (figs. 5.4b and 5.5b). Most of the average annual concentrations in the figures are discharge-weighted concentrations (method B in table 3.1, chapter III), which, when multiplied with annual water discharge, normally allows the calculation of realistic annual fluxes for dissolved nutrients. Only for the Po River, we took the values from the publication of Camusso et al. (2000) and do not know how the concentrations have been calculated.

For nitrate, it can be noted that the concentrations increased steadily from the beginning of the 1970s in all three rivers. Only since the beginning of the 1990s, the values seem to remain at more or les constant levels. The increase was more important in the Ebro and Po rivers than in the Rhone River. Also the annual nitrate loads increased on average in all three rivers. On the basis on linear correlation of the loads and time, it can be estimated that for the 1970 to 1995 period, the nitrate loads increased on average by about 10% per year in the Ebro River. In the Rhone and Po rivers, this increase was about 4% and 5% per year, respectively.

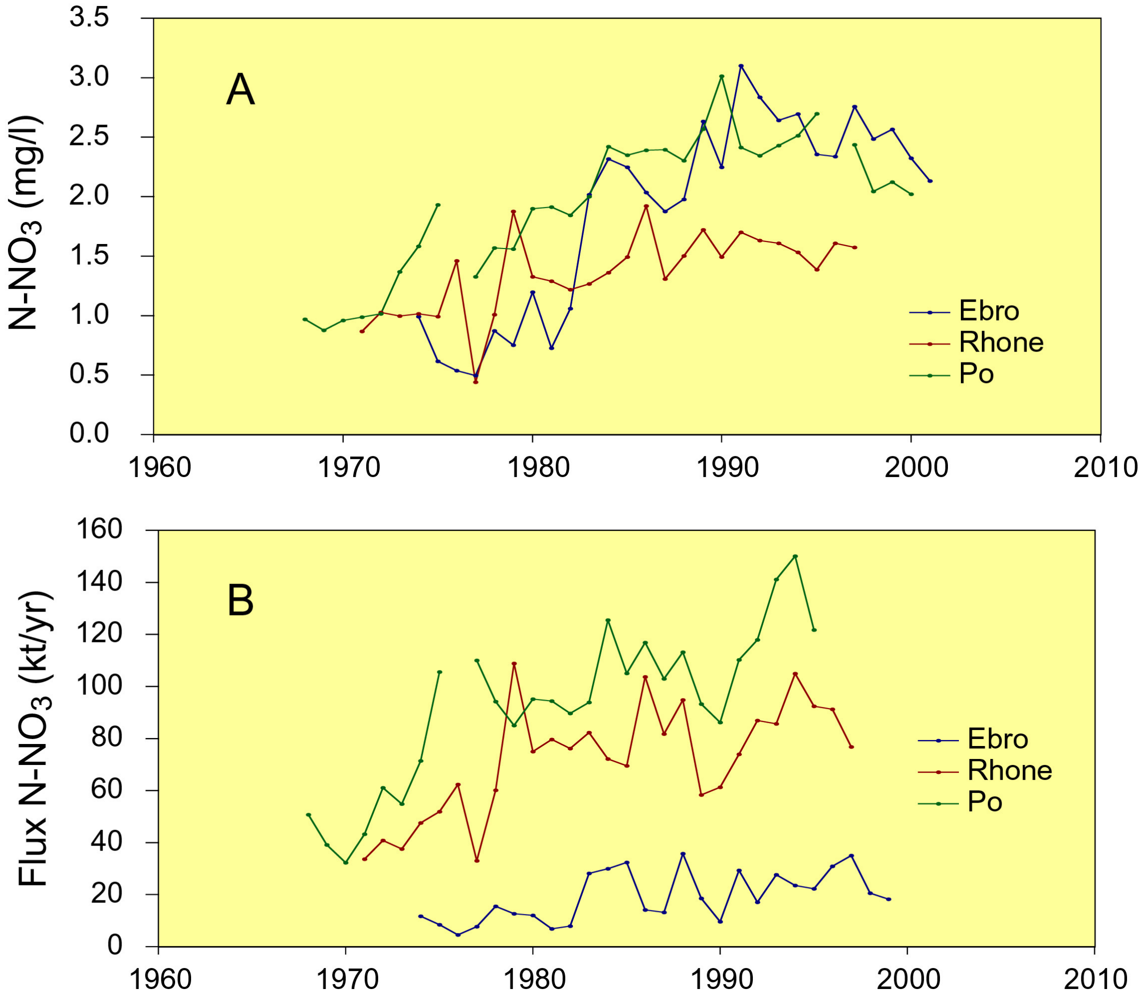

Fig. 5.4 *- Evolution of the average nitrate concentrations (A) and the annual nitrate loads (B) in the Po, Rhone and Ebro rivers during the last decades. The Po River data are from Camusso et al., (2000) for 1968 - 1995 and from the Po River Authority for 1997 to 2001. The Rhone River data are from Moutin et al. (1998) for 1971 - 1981 as well as from the French monitoring Agency "Agence de l'Eau Rhône - Méditerranée - Corse" (http://www.rdbrmc.com/) for 1981 - 1997. Finally, the Ebro River data are from Ibanez et al. (1995) for 1974 - 1986 and from the "Confederación Hidrográfica del Ebro" (http://www.oph.chebro.es/#). The sources for the water discharge data are described in chapter II.*

These trends are in good agreement with the situation in other European rivers. At many sites, annual concentrations are approaching a steady state, after two decades of rapid increase. This may reflect the use of nitrogen fertilisers and other changes in agricultural practices. Whereas the consumption of nitrogen fertilisers in Europe generally increased from 1970 to 1988, the consumption has decreased in recent years (Crouzet et al., 1999). However, this recent decrease mainly affects the rivers of western Europe, and the evolution of in the southern countries is less clear.

For phosphate, the trends are more diversified. There is also a strong increase of the phosphate concentrations in the Po, Rhone and Ebro rivers at the beginning of the 1970s, even more pronounced than in the case of nitrate. But about 10 to 20 years later, this evolution stops and the values started to decrease again. It is remarkable that in all three rivers, the phosphate concentrations at the end of the 1990s meet again the values that have been encountered at the beginning of the 1970s. When taking the mean of the phosphate loads in the three rivers, one can estimate that phosphate loads from 1975 to 1985 increased on average by about

15% per year. From 1985 to 1995, they then decreased again to about the initial values.

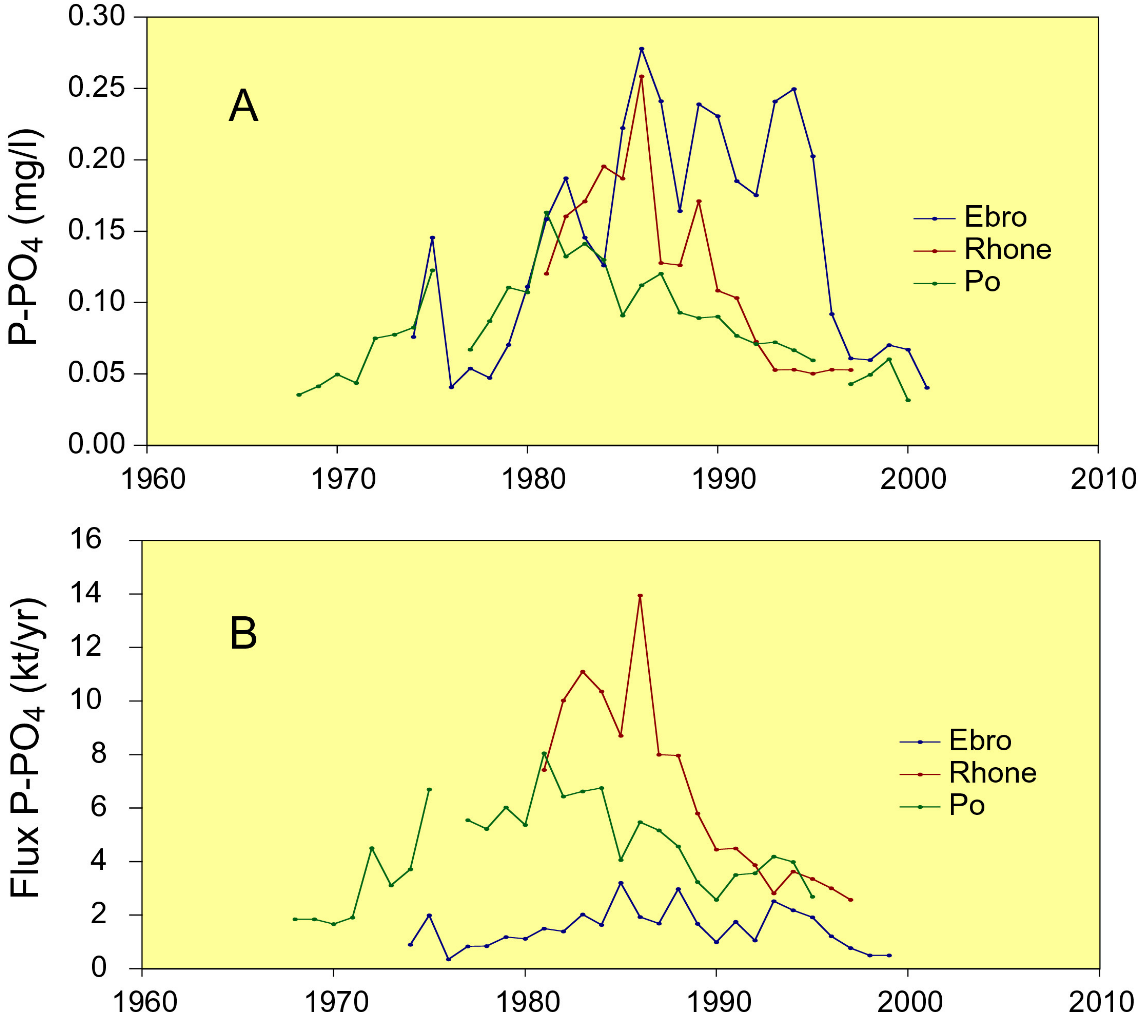

Fig. 5.5 *- Evolution of the average phosphate concentrations (A) and the annual phosphate loads (B) in the Po, Rhone and Ebro rivers during the last decades. For the data sources, see fig. 5.4*

But the evolution is not completely in phase between the three rivers, since the start of the decrease is different. This can be seen best when looking at the phosphate loads. The decline started earliest in the Po River (about 1980), followed then by the Rhone River (around 1985) and finally by the Ebro River (around 1993). The differences in the starting point of the phosphate decline may reflect the time lags in the launching of measures to defend phosphorous pollution in the different countries, such as the interdiction of the use of phosphorous detergents, and/ or differences in 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 in this river has been delayed by the multitude of reservoirs in this basin, which may have retained older phosphorous loads. Nevertheless, it has to be stated that the severe reduction of the riverine phosphorous loads is a widespread phenomenon in Europe. Phosphorous concentrations in EU and Accession country rivers generally declined by 30-40% during the 1990s, with greatest reductions in areas with formerly high phosphorous concentration. This is indicating that upgrading of wastewater treatment has been successful. Phosphorous load from industries has also been reduced due to the use of cleaner technology. But also here one can note that the evolution to better water quality is more rapid in western Europe than in southern Europe.

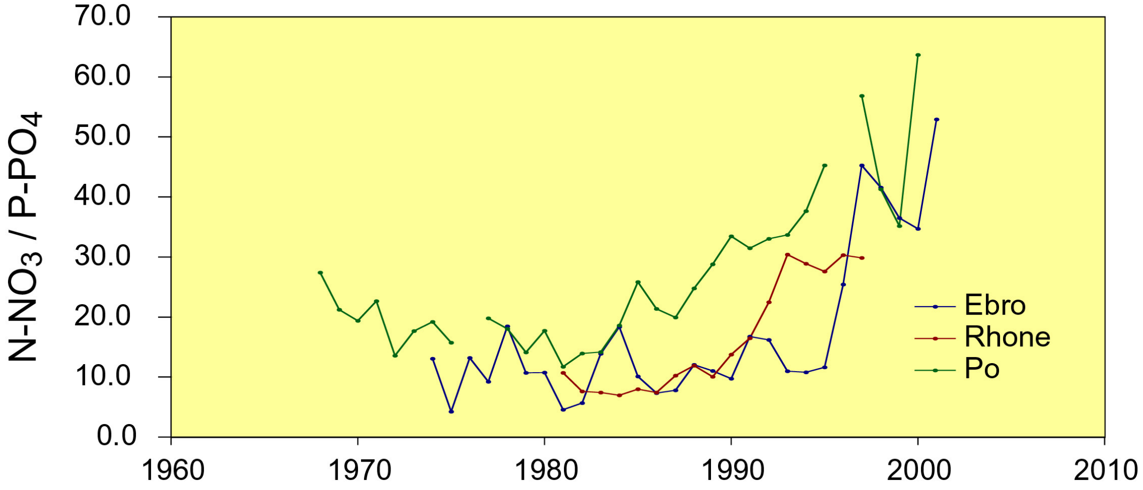

Fig. 5.6 - Evolution of the average nitrate to phosphate weight ratio (mg l^{-1} / mg l^{-1}) in the Po, Rhone and Ebro rivers during the last decades. For the data sources, see fig. 5.4.

Finally, it is worth being pointed out that, since the nitrate and phosphate concentrations did not follow the same evolutions, the composition of the riverine nutrient input to the Mediterranean Sea may have considerably changed during the last decades. Especially the nitrate to phosphate ratio changed remarkably (fig. 5.6). Whereas the weight ratio was about 10 to 20 during the 1970s and the beginning of the 1980s, it climbed up to values >40 in recent years. It is not excluded that this may not have had an impact on the biological systems in the marine environment.

5.4.2 – Coastal rivers in France

For comparison, we also present estimates for the evolutions of the nitrate and phosphate fluxes in some of the smaller coastal rivers in France (fig. 5.7). These rivers may be more typical for the Mediterranean region than the Rhone or the Po rivers, since they are entirely under Mediterranean climate. The data availability for these rivers was good and the fluxes could be determined in the same way as for the above-discussed large rivers. Mean annual nitrate fluxes did not show any detectable trend over the last 25 years, but this may also be due to the great inter-annual variability of discharge in these rivers, which can overprint the variability of the nutrient inputs to these rivers. Note that for the Tet River, for example, the inter-annual variability of water discharge varied within one order of magnitude (Serrat et al., 2001) from 1980 to 2000.

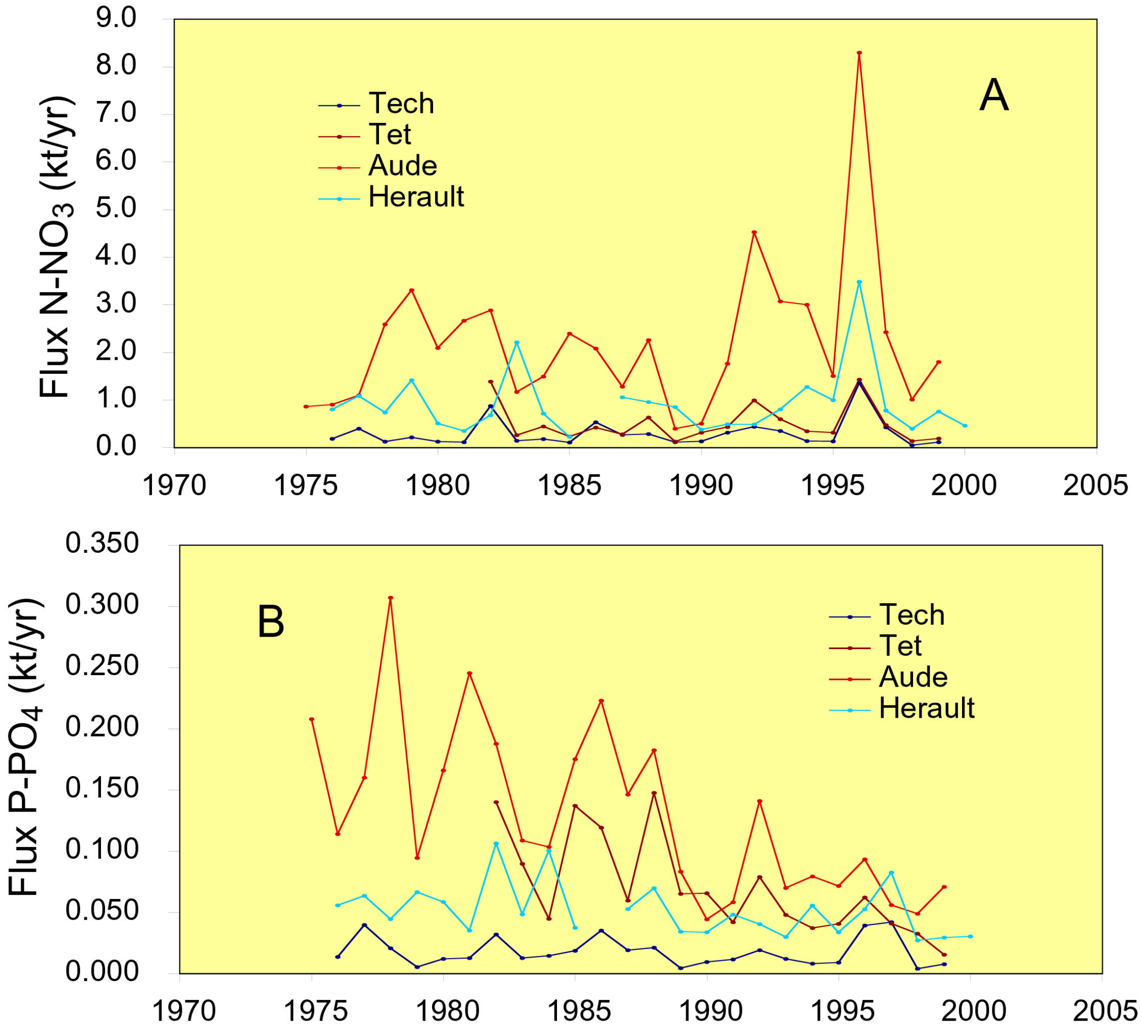

Fig. 5.7 - *Evolution of the nitrate (A) and phosphate (B) fluxes in some smaller coastal rivers in southern France. Data are from the French monitoring Agency "Agence de l'Eau Rhône - Méditerranée - Corse" (http://www.rdbrmc.com/).*

For phosphate, however, the mean annual fluxes decreased in most of the rivers over this period. The decrease is especially prominent with the beginning of the 1990s, in agreement with the data of the Rhone River (see above). It is probably mainly the ban and abandon of phosphate detergents that is responsible for this evolution.

5.4.3 – Other Mediterranean rivers

The data availability for trend analyses in the other Mediterranean rivers was less good than for the above-presented rivers. We found some additional data for the annual evolution of the nitrate and total phosphorous levels in some Greek, Italian and Croatian rivers, which are presented in the table 5.5. These data are annual arithmetic means, stretching over the period of 1980 to 1995. Since the corresponding annual water discharge was not available for all of these rivers, we did not calculate the corresponding nutrient fluxes.

Table 5.5 *- Evolution of the average nitrate and total phosphorous concentrations in some Mediterranean rivers (data from Kristensen, 1997).*

River	**Neretva**	**Nestos**	**Axios**	**Aliakmon**	**Pinios**	**Acheloos**	**Tiber**	**Arno**	**Adige**
Station	Opuzen	Drama	Saloniki	Kozani	Larissa	Agrinion	Ripetta	Calcinaia	Badia Bolesine
Country	Croatia	Greece	Greece	Greece	Greece	Greece	Italy	Italy	Italy
Year	Average nitrate concentration (mg $N\text{-}NO_3$/l)								
1980									
1981	0.174								
1982	0.154	1.009	0.984	0.434	1.364	0.075			
1983	0.027	1.039	1.093	0.321	1.501	0.099			
1984	0.270	1.253	1.156	0.352	1.258	0.122			
1985	0.123	1.152	1.524	0.208	1.438	0.106			
1986	0.321	1.720	1.800	0.580	1.671	0.242			
1987	0.410	1.836	1.734	0.585	1.847	0.129			1.576
1988	0.643	1.680	1.745	0.273	1.892	0.160			1.806
1989	0.728	1.594	1.628	0.336	1.231	0.172			1.355
1990	0.557	0.779	1.939	0.191	3.012	0.346		5.138	1.207
1991		0.856	1.891	0.764	2.003	0.246		2.549	1.336
1992		0.708	1.935	0.303	1.521	0.165		3.165	0.207
1993		0.703	2.084	0.480	1.423	0.228		2.558	1.374
1994		1.067	2.370	1.174	2.256	0.339		2.464	1.422
1995					0.421			0.488	1.710
Year	Average total phosphorous concentration (mg P/l)								
1980	0.026								
1981	0.062								
1982	0.041	0.100	0.330	0.020	0.060	0.010			
1983	0.022	0.150	0.410	0.010	0.070	0.005	0.300		
1984	0.033	0.160	0.330	0.010	0.060	0.030			
1985	0.037	0.150	0.610	0.030	0.080	0.005	0.300		
1986	0.036	0.100	0.490	0.020	0.100	0.010			
1987	0.111	0.170	0.540	0.020	0.070	0.020			0.150
1988	0.030	0.170	0.930	0.020	0.060	0.005	0.370		0.180
1989	0.028	0.110	0.500	0.010	0.050	0.010	0.300	0.380	0.100
1990	0.018	0.122	1.012	0.014	0.069	0.005	0.601	0.693	0.125
1991		0.080	0.541	0.016	0.071	0.061	0.256	0.233	0.050
1992		0.080	0.626	0.015	0.083	0.005		0.319	0.058
1993		0.065	0.988	0.008	0.079	0.015		0.118	0.043
1994		0.054	0.628	0.030	0.079	0.018		0.139	0.133
1995								0.167	0.049

For nitrate, most of the rivers evolved towards greater nitrate concentrations (e.g., the rivers Neretva, Axios, Acheloos), or do not show any clear trend (e.g., the rivers Pinios, Adige). Only in the Arno River, nitrate decreased considerably from 1990 to 1995. The average concentrations were the highest in this river, indicating that a considerable part of the nitrate load may originate from point source pollution. Nitrate decrease can therefore be related to the general improvement of the water quality in this river.

For total phosphorous, most of the rivers depict decreasing values over time (e.g., the rivers Neretva, Nestos, Arno, Adige) or have no trend (e.g., the rivers Aliakmon, Acheloos). The decrease is the most significant since the second half of the 1980 for the Italian rivers, which is in good agreement with the evolution in the Po River. The only river where the total phosphorous concentrations increased is the

Axios in Greece. It is also this river that depicts the highest phosphorous level. Apparently, no measures to limit phosphorous pollution were undertaken for this river in Macedonia, where most of the Axios drainage basin is situated. This confirms the general picture that, although phosphorous pollution is broadly reduced, the improvement is not uniformly progressing in the different countries of the Mediterranean.

5.5 – Budgets

5.5.1 – Global N and P inputs to the Mediterranean Sea

Even if the above-presented nutrient data are incomplete with respect to the spatial and temporal variability of the riverine nutrient loads, they are sufficient to allow a general extrapolation of global budgets for the nitrogen and phosphorous inputs to the Mediterranean Sea. To do so, we assumed that the median N and P concentrations in table 5.4 are representative for the Mediterranean rivers on the whole, and retained the values of 1.25 mg N/l, 0.1 mg P/l and 0.25 mg P/l for the mean $N\text{-}NO_3$, $P\text{-}PO_4$ and TP concentrations, respectively. The year 1985 was attributed to these values as corresponding reference period, which means that the overall water discharge may have been in the range of 375 km^3/yr (see chapter II). The resulting fluxes were hence 469 kt $N\text{-}NO_3$, 38 kt $P\text{-}PO_4$ and 94 kt TP (table 5.6). For the other N and P species, we did not attribute any flux estimates because of the scarceness of our data. But one may retain that the other inorganic nitrogen species (NO_2 and NH_4) are normally only about 10% of the nitrate concentrations, and the total DIN flux for 1985 should be in the range of 520 kt N.

When combining these estimates with the trends discussed above, it is also possible to reconstruct the temporal evolution of these nutrient fluxes. For this, we assumed that the trends in the Po, Rhone and Ebro rivers are representative for the entire Mediterranean area. This means that the nitrate fluxes may almost have doubled from about 1975 to 1995, whereas the phosphorous fluxes increased rapidly from about 1975 to 1985, and decreased then again to about the initial values. The table 5.6 therefore also resumes the corresponding total nutrient fluxes for these periods. Because of the lack of data, we also assumed that the evolution of total phosphorous entirely followed the evolution of phosphate, although this has, of course, not necessarily to be the case.

***Table 5.6** - Estimated evolution of the total riverine nutrient fluxes to the Mediterranean Sea*

	Flux $N\text{-}NO_3$ (kt N/ yr)	Flux $P\text{-}PO_4$ (kt P/ yr)	Flux TP (kt / yr)	$N\text{-}NO_3$/ $P\text{-}PO_4$
<1975	333	14	36	23.4
1985-90	469	38	94	12.5
>1995	605	14	36	42.4

It is evident that the mentioned reference years shouldn't be taken literally; they rather represent time slices of several years more or less situated around the indicated calendar years. Especially for the phosphorous fluxes, the recent decrease of the values may have been less rapid in several countries, as demonstrated above. But this means only that the values in table 5.6 should have been attained later than indicated. In our scenario, we therefore propose that the 1995 situation is still valid for today. Note that also the nitrate increase seems to stop in recent years, confirming this assumption.

The values we extrapolated compare well with other estimates. On the basis of a modelling approach, Seizinger and Kroetze (1998) calculated for the DIN input to the Mediterranean Sea in 1990 values of about 530 to 710 kt N/yr, depending on the method they used. Béthoux et al. (1998) proposed that the DIN input over the 1971-1988 period may have been in the range of 350 kt N/yr. These estimates are not very different from ours. Only for phosphorous, the latter authors found much greater values, that is about 185 kt P/yr for TP and 48 kt P/yr for P-PO_4. It is clear that due to the greater variability of the phosphorous levels in our data collection, more uncertainty has to be associated with the P fluxes. But we feel that especially the value for TP of Béthoux et al. (1998) may be somewhat too large, not at least because of the reduction of the particulate fluxes on the whole as a result of the river damming (chapter III), which also should affect the TP fluxes.

5.5.2 – Modelling

The close coupling of the riverine nutrient levels with the human activities in the river basins also allows extrapolating the nutrient budgets as a function of economic and demographic data. Especially for DIN, it has been demonstrated that the riverine export rates are first of all a function of the population density in the basins (Caraco and Cole, 1998; Seizinger and Kroetze, 1998). Also our data confirm this for the Mediterranean region, allowing a refinement of our nitrate budgets at regional scales. In table 5.7 we present our best estimates for the average nitrate concentrations in the rivers of the Mediterranean countries for which we found data. These values correspond to the median values of table 5.4, but in some case we adjusted them subjectively according to the river sizes in the different countries whenever large differences are present (such as in France). It can be shown that these national averages (C_n; mg N/l) are highly correlated to the ratio of the Mediterranean population densities (Mpop; inh/km^2) and the average drainage intensities (Q; mm) in these countries. The following equation describes the relationship:

$$C_n = -0.1843\,[\log(Mpop/Q)]^2 + 1.0089\,\log(Mpop/Q) + 1.7783 \quad \text{(iii)}$$

$$R^2 = 0.92,\ n = 8$$

With equation (iii), a theoretical national nitrate concentration can be determined for each Mediterranean country, and by multiplying this with the average runoff from these countries, also the corresponding nitrate flux (table 5.7). This results in an overall nitrate input to the Mediterranean Sea of 490 kt N/yr for 1985, which is in good agreement with our first estimate. According to our scenario, about 40% of the total input comes from Italy. The next important countries are France (15%), Greece (10%), Turkey (9%) and Spain (7%).

Table 5.7 *- Estimated nitrate export by country to the Mediterranean Sea in 1985 (for further explanation, see text).*

Country	Area (10^3 km^2)	Q-85* (km^3/yr)	Popd** (inh/km^2)	N-NO$_3$ (mg/l) estimated	modelled	N-flux (kt/yr)
Albania	30	21.9	146	0.7	1.0	21.7
Algeria	100	3.7	222		2.4	9.1
Cyprus	9	1.3	54		1.3	1.7
Egypt	2920	10.1	209	3.0	3.0	30.2
France	131	66.3	124	1.2	1.1	72.6
Greece	171	36.6	92	1.4	1.4	50.6
Israel	10	0.3	784		2.8	0.9
Italy	301	144.2	198	1.8	1.4	196.8
Libya	7	0.8	25		1.1	0.8
Morocco	63	1.9	88		2.2	4.1
Spain	182	18.0	166	1.9	2.0	35.9
Syria	6	0.7	326		2.2	1.5
Tunisia	34	0.9	135		2.4	2.2
Turkey	154	31.2	92	1.2	1.4	44.0
Yougoslavia	55	37.8	57	0.5	0.5	17.8
total						490.0

* Estimated runoff in 1985 (see chapter II).

** Population density in the Mediterranean part of the countries (see tab. 1.2 in chapter I)

For phosphorous, no extrapolation approach based on socio-demographic and economic data can be developed. Phosphorous levels are much more depending on point source pollution, which are difficult to be modelled.

Chapter VI – Heavy metals

6.1 - Introduction

Several definitions of the term "heavy metals" are used in the scientific literature, but the main meaning is metals that have a density greater than 4 or 5 g/cm^3. This term includes those metals from the periodic table groups IIA through VIA. The semi-metallic elements (metalloids) boron, arsenic, selenium, and tellurium are often included in this classification. Morgan and Stumm (1991) suggest a list of 14 hazardous metals and metalloids which are listed in table 6.1.

Table 6.1 *- Chemical elements considered as heavy metals (Morgan and Stumm, 1991)*

Chromium (Cr)	Copper (Cu)	Zinc (Zn)
Arsenic (As)	Selenium (Se)	Silver (Ag)
Cadmium (Cd)	Indium (In)	Tin (Sn)
Antimony (Sb)	Mercury (Hg)	Thallium (Tl)
Lead (Pb)	Bismuth (Bi)	

However, nowadays the common meaning of heavy metals is based on environmental behaviour or toxicological characteristics: heavy metals are all metals or metalloids with acknowledged hazards for health or environment. They are stable and persistent environmental contaminants since they cannot be degraded or destroyed. At trace levels, many of these elements are necessary to support life. However, at elevated levels they can affect marine biota and pose risk to human consumers of seafood. The most problematic heavy metals for the environment are mercury, cadmium, lead and arsenic. A list of effects caused by certain heavy metals on the environment is given in table 6.2.

Unlike persistent organic pollutants, metals accumulate in protein tissues and bone rather than in the fat of animals. Many organisms are able to regulate the metal concentration in their tissues. Fish and crustacean can excrete essential metals such as copper or zinc, if they are present in excess. Some can also partially excrete non-essential metals such as mercury and cadmium. But plants and bivalves are not able to successfully regulate metal uptake. This is why bivalves often serve as biomonitor organisms in areas of suspected pollution. Plants are usually equally or less sensitive to cadmium, mercury, lead, zinc and nickel than fish and aquatic invertebrates.

***Table 6.2** - Harmful effects of some heavy metals on the environment (according to the web-site http://heavy-metals.gpa.unep.org/).*

Cadmium	Critical effects of cadmium contamination on plants are a decrease in productiveness, reduced rates of photosynthesis and transpiration, and altered enzymatic activities. In sea waters, cadmium levels greater than 7 mg l-1 can initiate toxic effects for animals, including growth retardation and decrease survival of invertebrates, and kidney damage and decalcification of the skeleton for higher marine animals and seabirds.
Mercury	The major toxic action of mercury is the inhibition of enzymatic processes, which can affect the reproduction and the nervous system of birds and mammals. In fish, the effects of mercury also include a decreased of sense of smell, damage to gills and blindness. High concentrations of mercury lead to reduced growth of plants. One important hazardous effect of mercury in the aquatic environment is that it biomagnifies in the food chain.
Lead	Effects of lead on plants are limited to areas where relatively high concentrations of lead are found, like areas near mines or smelters. For animals, the signs for lead poisoning are central nervous system disorders, high excitivity, motor abnormalities and blindness. In fish, lead accumulates primarily in gills, liver, kidney and bones, causing blackening of the tail, damage to the spine and reducing larvae survival.
Zinc & copper	Zinc and copper constitute hazard to aquatic life in polluted waters where other much more hazardous metals like lead, mercury, cadmium are also present because its toxicity with the other metals is additive. It has been reported that sublethal concentrations of Zn impair the reproduction of salmon and some marine invertebrates.

6.2 - Sources

6.2.1 - Natural sources

Rocks and sediments contain naturally metallic elements (tab. 6.3). With the mechanical erosion and the chemical alteration of these rocks, a part of the metals become available for plants and animals in soils and water. Locally, the concentrations of heavy elements in rocks may vary by several orders of magnitude depending on the rock type. Rocks that contain metallic ores, such as certain igneous rocks, have much higher concentrations. Ore deposits of metals are made up of oxides and especially sulphurous minerals, which are often very reactive in surface conditions. They can be easily dissolved by rain or surface waters and have an important capacity of acidification. Even if these ores are not exploited by the mining industry, they can contaminate underground and surface waters and have adverse effects.

In environmental studies on heavy metals, an important difficulty is the distinction between the natural local background and the input from human activities. In cases of high pollution, the sources are often precise and easily identified. But if natural and anthropogenic sources are diffused, it can be difficult to quantify the respective contribution of each source. Several regional studies show that the natural concentrations for a heavy metal in surface water may be higher than the recommended values or guidelines for drinking water. Such "natural pollution" may have disastrous effects on human health. In Bangladesh and West Bengal, alluvial Ganges aquifers used (since the 1970s) for public water supply are polluted with naturally occurring arsenic. Several million people are at risk of exposure to arsenic, and 2 to 10 thousand are suffering of arsenicosis (UNEP 1999).

Table 6.3 *- Average heavy metal concentrations in the Earth's crust (Wedepohl, 1991). The unit is mg/kg.*

Metals	Cr	Ni	Cu	Zn	As	Ag	Cd	Sn	Hg	Pb
Continental crust	88	45	35	68	3.4	0.10	0.10	2.5	0.02	15
Oceanic crust	317	144	81	78	1.5	0.03	0.13	0.9	0.02	0.89

6.2.2 - Pollution sources

Emissions of heavy metals in relation with the human activities are of two types: emissions from diffuse sources, such as automobiles, and emissions from stationary sources (e.g. industry, waste disposal).

Diffuse sources are especially important in urban areas. The concentrations of heavy metals in street dust decrease rapidly from areas with high traffic density to mid-urban and rural areas. Typical inner city abundance in street dust for lead are 1000-10000 mg/kg; in rural areas these abundance are between 30 and 500 mg/kg (Fergusson, 1990). Main heavy metals involved in urban dust are lead (Pb) and cadmium (Cd). Some high concentrations of lead in urban house dust suggest that the two major sources of lead are automobile emissions and lead containing paint. Cadmium occurs in rubber because of its chemical and mineralogical association with zinc; zinc compounds are used in vulcanising. That is why the dust from rubber tyres is the main sources of cadmium in street dust: usually between 0.1 and 2 mg/kg.

For stationary sources, heavy metals are released as a result of a number of industrial and other activities. Waste disposal appears to be, in the United States, the most significant hazardous source of heavy metals in the environment with important risks for ground and surface waters. Metal finishing, chemical industries, mining and ore processing are also major ways to emit heavy metals in the atmosphere, in surface and ground waters.

6.3 - Transport in rivers

The abundance of heavy metals in a river depends not only the natural and anthropogenic sources in the watershed, but also on the chemical and physical properties of the river, such as acidity (pH), oxydo-reduction conditions (Eh), turbidity (suspended load), colloids and organic matter particles. These factors may drastically change along the watercourse due to the season or other climatic effects (storm, dryness). That is why, in order to address the problems of pollution and pollutant transport in rivers, the monitoring of physical and chemical properties is very important.

Under the usual pH conditions in rivers (pH range of 7 - 8.5), the main part of heavy metals (Cd, Pb, Zn, Cu, Hg) are not dissolved but they are adsorbed on the surface of the suspended particles. This is why the particulate phase is normally by far the dominant transport form for heavy metals in rivers (tab. 6.4). Absorption can be especially important on the smallest fraction, which are the colloids (< 0.45 µm). These colloids are mainly composed of hydrous oxides of iron, aluminium, manganese and organic matter. The distinction between the dissolved and adsorbed fractions of an element is important in addressing the problems of transport, bio availability and remediation. In case of acidification, metallic elements are desorbed from surfaces. Colloids may be dissolved too, which increases the concentrations of dissolved metals. Extreme cases are some surface waters from mining areas which are very acid (pH = 2-3). In such waters, the concentrations of heavy metals may be 2 to 5 orders of magnitude higher than in the unpolluted surface waters (source: http://www.infomine.com/).

Table 6.4 *- Proportion of heavy metal loads associated to particulate matter in the Po and the Rhone rivers in % of the total loads.*

	Al	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Po River	98.4	23.0	41.0	94.7	88.2	73.0	88.0	78.4	93.1	71.1
Rhone River	--	--	90.0	--	99.0	87.4	99.0	93.5	99.0	94.0

Data sources: Pettine et al. (1991, 1994, 1997) for the Po River; Pont (1996) and Chiffoleau et al. (1995) for the Rhone River (the latter has been sampled during a high turbid year).

Finally, it is worth mentioning that Mercury and Arsenic have noticeable behaviour in freshwater. The principal form of mercury in freshwater is Hg^{2+} dissolved or adsorbed on particles. But bacteria and microbes can transform Hg^{2+} to methyl-mercury, the most toxic form of mercury, which accumulates in fish and shellfish. That is why most mercury in animals and humans is methyl-mercury. Arsenic is a metalloid with different chemical properties than the metallic elements such as Cu, Zn, Cd or Hg. In surface waters, arsenic (As (V)) forms chemical complexes with hydroxide groups. Because of the formation of these complexes, arsenic is not adsorbed on suspended particles in the same way as other heavy metals (see also tab. 6.4). Moreover, arsenic has two oxidation states: As (III) and As (V). Each form has its own behaviour in natural systems. In surface and oxygenated waters, like river waters, As (V) is usually dominant. In more confined and less oxygenated systems, As (III) may be the principal form of arsenic. These are the reasons why the behaviour of arsenic in natural systems is often difficult to predict. Numerous works are actually in progress about environmental chemistry, bio toxicity and remediation of arsenic.

6.4 - Heavy metals in Mediterranean rivers

An assessment of the average metal contents and loads in Mediterranean rivers is more difficult for heavy metals than for other pollutants, such as nutrients, because it can hardly rely on the data regularly collected by national monitoring programs. Two reasons are responsible for that. On the one hand, many monitoring programs only measure total metals without filtering the sample, although the utility of his information is restricted. As we have seen above, by far most of the heavy metal transport occurs in the particulate phase, and a spatial and temporal inter-comparison of data requires a sampling strategy that is representative for the total suspended sediment transport. This is almost impossible with the sampling frequency normally applied by national monitoring agencies (see chapter III). Including one high-turbid sample or not in a data set may completely change the resulting averages.

Table 6.5 *- Variability of metal contents over one year: example of the Rhone River (from Pont, 1996, and Chiffoleau et al., 1995).*

Ratio	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	A - Dissolved metal concentration (µg/l)						
Max / min	7.6	19	3.4	12	22	4.9	9.2
Std-dev./ mean	0.44	0.38	0.27	0.57	0.17	0.35	0.49
	B - Particulate metal content (µg/g)						
Max / min	7.5	2.9	3.75	19.5	>55	7.2	>300
Std-dev./ mean	0.45	0.22	0.31	0.85	0.33	0.41	0.59
	C - Total metal concentration in 1l of unfiltered water (µg/l)						
Max / min	38	264	50	1680	211	145	98
Std-dev./ mean	1.5	2.4	1.8	2.8	2.5	1.8	2.0

Total number of analyses: 32 to 35 for the hydrological year 1994/95 (average Q = 2850 m^3/s)

On the other hand, one has also to point out that the contamination problem is still a major problem for the analysis of heavy metals. National monitoring agencies usually charge public laboratories for the analytics, doing in routine great number of samples of different origins. In fact, the analysis of drinking or surface water may be followed by the analysis of waste water or sewage sludge in the same place with the same instrument, which can lead to a great deal of invalid data and misinterpretation of the environmental process (Bortoli et al., 1998).

For these reasons, we refer in this study mainly to studies that were taken out by independent research institutions, applying ultra-clean techniques for the analytics. In the following, we only present data for dissolved and particulate metals (in µg/l and µg/g, respectively), but avoided data for total metals in µg/l. The variability of this parameter is often too large for being representative for one river (tab. 6.5). Referring the particulate metal content to one gram of suspended sediments is a better mean to assess the pollution state of a river than referring it to one litre of water. This does, of course, only allow flux calculations if the corresponding fluxes of total suspended solids are known.

6.4.1 - Particulate metals

The average heavy metal contents in the total suspended solids for 17 different Mediterranean rivers are presented in table 6.6. As for nutrients (see previous chapter), we also presented the reference periods corresponding to the data whenever this information was available. The median concentrations for all rivers are about 1, 51, 0.3, 30, 68 and 212 µg/g for the elements Cd, Cu, Hg, Ni, Pb and Zn, respectively. These values witness a general impact of pollution in the Mediterranean rivers: when dividing them by the averages for the composition of continental crust (tab. 6.3), most of the ratios are greater than 1 (tab. 6.7). The highest ratios are found for the elements Hg, Cd, and Pb, indicating that these elements are mostly derived by anthropogenic pollution.

However, when compared to the Seine or the Rhine rivers, one has to note that the heavy metal concentrations are often two to three times lower in the Mediterranean rivers. Hence, the pollution is less important compared to the highly industrialised river basins in northwestern Europe (tab. 6.8).

For individual rivers, certain particularities can de detected in the relative abundance of the trace metals. Elevated concentration from pollution sources may be present in the following rivers for the following elements: Acheloos (Ni, Zn) Adige and Bradano (both Cd), Ebro (Cr, Cu, Cd), Goksu (Cr), Herault (As, Cu, Pb), Orb (Cu, As), and Tiber (Cd, Cu, Zn). For the Martil River in Morocco, only few elements were analysed, showing highest pollution levels for Pb and Zn. It is evident that not in all cases, pollution alone must be responsible for elevated heavy metal concentrations. The values should be interpreted together with the geological and lithological patterns of the rivers drainage basins, which is, of course, beyond the scope of this study. In the Po and Rhone rivers, the heavy metal concentrations are elevated for almost all of the elements (Cd, Cr, Cu, Hg, Zn (Po), Pb (Rhone), Ni), with generally greater values for the Po than for the Rhone. The lowest values were found in the Var and Argens rivers in France. Here, the natural background levels probably mainly control the heavy metal concentrations in the sediments.

***Table 6.6** – Average concentrations of particulate trace metals (µg/g) in some Mediterranean rivers (for source indexes, see reference list)*

Rivers	Country	As			Cd			Cr			Cu			Hg			Ni			Pb			Zn		
		µg/g	period	*source*	*µg/g*	period	*source*	*µg/g*	period	*source*	*µg/g*	period	*source*	*µg/g*	period	*source*	*µg/g*	period	*source*	*µg/g*	period	*source*	*µg/g*	period	*source*
ADIGE	Italy				1.6	88-90	*91.109*				50.0	88-90	*91.109*				32.0	88-90	*91.109*	49.0	88-90	*91.109*	270	88-90	*91.109*
					1.9	85	*91.110*				75.0	85	*91.110*							72.0	85	*91.110*			
		25.3	95-96	*98.003*	1.2	95-96	*98.003*	60.7	95-96	*98.003*	76.6	95-96	*98.003*				44.6	95-96	*98.003*	72.7	95-96	*98.003*	212	95-96	*98.003*
AKHELOOS	Greece										50.5	82-90	*97.021*				418.0	82-90	*97.021*	40.4	82-90	*97.021*	470	82-90	*97.021*
ARGENS	France	4.2	94-95	*97.006*	0.1	94-95	*97.006*	15.6	94-95	*97.006*	3.2	94-95	*97.006*	<0.03	94-95	*97.006*	9.7	94-95	*97.006*	19.6	94-95	*97.006*	38	94-95	*97.006*
ARNO	Italy							159.0	88-90	*91.109*															
BRADANO	Italy				2.6	85	*91.110*																		
BRENTA	Italy																			145.0	85	*91.110*			
CEYHAN	Turkey										<10.0		*94.066*				<20.0		*94.066*						
EBRO	Spain	6.1		*91.105*	1.8		*91.105*	215.0		*91.105*	71.0		*91.106*				19.0		*91.106*	60.0		*91.106*			
GOKSU	Turkey				0.5		*92.063*	270.0		*92.063*	16.8		*92.063*							5.0		*92.063*	27		*92.063*
HERAULT	France	26.4	94-95	*97.006*	0.7	94-95	*97.006*	33.6	94-95	*97.006*	57.2	94-95	*97.006*	0.14	94-95	*97.006*	24.3	94-95	*97.006*	129.0	94-95	*97.006*	279	94-95	*97.006*
MARTIL	Morocco							91.0		*97.020*										517.0	94-95	*97.020*	438	94-95	*97.020*
ORB	France	28.7	94-95	*97.006*	0.1	94-95	*97.006*	37.5	94-95	*97.006*	132.0	94-95	*97.006*	0.29	94-95	*97.006*	30.2	94-95	*97.006*	68.4	94-95	*97.006*	138	94-95	*97.006*
PO	Italy	7.0	88-90	*94.001*	1.7	88-90	*94.001*	124.0	88-90	*94.001*	75.0	88-90	*94.001*	1.54		*91.109*	112.0	88-90	*94.001*	75.0	88-90	*94.001*	342	88-90	*94.001*
		5.6	92-95	*97.016*				31.2	92-95	*97.016*															
RHONE	France	13.2	94-95	*97.006*	1.8		*91.105*	102.0	94-95	*96.032*	41.6	94-95	*96.032*	0.47	94-95	*96.032*	31.9	94-95	*96.032*	32.9	94-95	*96.032*	108	94-95	*96.032*
					0.7	94-95	*96.032*	155.0		*91.105*	125.0		*91.105*	0.30		*94.068*	60.0		*91.105*	120.0		*91.105*	230		*94.068*
					0.7		*94.068*	110.0		*94.068*	80.0		*94.068*	1.14	94-95	*97.006*	52.0		*94.068*	80.0		*94.068*	95	94-95	*97.006*
					1.0	94-95	*97.006*	39.6	94-95	*97.006*	26.0	94-95	*97.006*	0.48		*96.022*	28.8	94-95	*97.006*	30.0	94-95	*97.006*			
SEYHAN	Turkey										<10.0		*94.066*				< 20.0		*94.066*						
TIBER	Italy				2.0	88-90	*89.109*				100.0	88-90	*89.109*							130.0	88-90	*89.109*	280	88-90	*89.109*
VAR	France	7.7	94-95	*97.006*	0.1	94-95	*97.006*	19.8	94-95	*97.006*	17.1	94-95	*97.006*	0.04	94-95	*97.006*	14.2	94-95	*97.006*	11.9	94-95	*97.006*	47	94-95	*97.006*
					0.4		*92.063*				25.0		*92.063*							5.6		*92.063*	68		*92.063*

Table 6.7 *– Ratios of the average particulate metal concentration in different Mediterranean rivers of table 6.3 over the average composition of the continental crust in table 6.3.*

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Median – all Med. rivers	2.3	10.0	1.0	1.4	15.0	0.7	4.6	3.1
Median - Po	1.9	17.0	0.9	2.1	77.0	2.5	5.0	5.0
Median - Rhone	3.9	8.5	1.2	1.7	23.8	0.9	3.8	1.6
Median - Ebro	1.8	18.0	2.4	2.0		0.4	4.0	

Table 6.8 *– Particulate metals in selected world rivers measured by ultra clean techniques (from various sources collected by Cossa et al., 1993, 1996)*

	Cd (μg/g)	Cu (μg/g)	Hg (μg/g)	Ni (μg/g)	Pb (μg/g)	Zn (μg/g)
Impacted rivers - Europe						
Rhine	2.7	100	1.46	--	129	588
Scheldt	12.0	70-150	--	--	--	--
Seine	5.0	174	1.22	--	184	611
Impacted rivers - North America						
St. Lawrence	2.2	--	--	--	134	272
Niagara	5.6	6.4	1.57	--	93	313
Non-impacted rivers						
Lena	--	28	0.13	--	23	143
Ob	--	--	0.05	--	--	--
Amazon	--	--	--	--	--	--
Yenissei	--	--	0.04	--	--	--

6.4.2 - Dissolved metals

Table 6.9 represents the average dissolved trace metal concentrations for 13 Mediterranean rivers; the values in table 6.10 allow the comparison with other world rivers. Elevated levels were mainly found in some Italian rivers, such as the Po (Cd, Cu, Ni, Zn), the Tiber (Pb, Zn) and the Arno rivers (Cd), although a direct comparison is not always possible because of the differences in the reference periods corresponding to the values. Also the Ebro River seems to have somewhat elevated Cd values. By far the lowest values were found in the Krka River in Croatia, confirming the pristine state of this river (see also the other chapters).

***Table 6.9** – Average concentrations of dissolved trace metals (µg/l) in some Mediterranean rivers (data in brackets: ultra clean techniques doubtful; for source indexes, see reference list)*

Rivers	Country	As			Cd			Cr			Cu			Hg			Ni			Pb			Zn		
		µg/l	period	*source*	*µg/l*	period	*source*	*µg/l*	period	*source*	*µg/l*	period	*source*	*µg/l*	period	*source*	*µg/l*	period	*source*	*µg/*	period	*source*	*µg/*	period	*source*
ADIGE	Italy				0.032	88-90	*91.109*				2.39	88-90	*91.109*							0.74	88-90	*91.109*			
		1.44	95-96	*98.003*	0.040	95-96	*98.003*	0.17	95-96	*98.003*	1.05	95-96	*98.003*				0.82	95-96	*98.003*	0.19	95-96	*98.003*	2.53	95-96	*98.003*
AKHELOOS	Greece										0.33	82-90	*97.021*				1.46	82-90	*97.021*	0.29	82-90	*97.021*	(2.6)	82-90	*97.021*
ALIAKMON	Greece										(10.5)	86-88	*90.001*							(7.5)	86-88	*90.001*	(50.5)	86-88	*90.001*
ARNO	Italy				0.020	88-90	*89.109*				2.00	88-90	*89.109*	0.07	88-90	*89.109*				1.00	88-90	*89.109*			
					0.100		*89.116*				1.75		*89.116*							0.21		*89.116*			
AXIOS	Greece										(7.0)	86-88	*90.001*							(8.0)	86-88	*90.001*	(67.3)	86-88	*90.001*
BRADANO	Italy				0.076	85	*91.110*																		
BRENTA	Italy										2.54	85	*91.110*							0.50	85	*91.110*			
EBRO	Spain				0.015		*91.106*				1.30		*91.106*				1.25		*91.106*	0.025		*91.106*	0.55		*91.106*
					0.061		*92.065*				1.80		*92.065*				1.50		*92.065*	0.030		*92.065*	0.60		*92.065*
					0.120		*89.116*				0.97		*89.116*				1.18		*89.116*	0.155		*89.116*			
KRKA	Croatia	0.1	86-87	*91.108*	0.005		*92.065*				0.10		*89.116*	0.0004		*96.022*	0.10		*92.065*	0.010		*92.065*			
					0.010		*89.116*													0.083		*89.116*			
NILE	Egypt				0.008		*89.116*				0.95		*89.116*							0.034		*89.116*			
PO	Italy	0.41	88-90	*91.109*	0.110	88-90	*94.001*	1.10	88-90	*94.001*	2.07	88-90	*94.001*	0.009	88-90	*91.109*	2.07	88-90	*94.001*	0.260	88-90	*91.109*	6.65	88-90	*94.001*
		1.50	92-95	*97.016*	0.065		*92.065*	1.40	93-95	*97.016*	1.63		*89.116*				3.30		*92.065*	0.148		*92.065*			
		1.34	88-90	*94.001*							1.50		*92.065*							0.150		*89.116*			
																				0.280		*94.001*			
RHONE	France				0.028		*92.065*	0.274	94-95	*96.032*	0.02	94-95	*96.032*	0.001	94-96	*96.032*	0.86	94-95	*96.032*	0.045	94-95	*96.032*	1.14	94-95	*96.032*
					0.050		*89.116*				1.93		*89.116*	0.018		*92.065*	1.40		*92.065*	0.083		*92.065*	1.30		*92.065*
											2.20		*92.065*	0.001		*96.022*				0.090		*89.116*			
TIBER	Italy				0.080	88-90	*91.109*				0.90	88-90	*91.109*	0.020	88-90	*91.109*				0.40	88-90	*91.109*	5.30	88-90	*91.109*
					0.015		*89.116*																		

It is worth noting that, contrarily to the particulate metals, there is no fundamental difference between the Mediterranean and the north western European and American rivers. Since the concentrations can be strongly controlled by the chemical and physical properties of the river water (pH, Eh, etc.), it is possible that the dissolved metals may be less indicative for an assessment of the pollution state of a river.

***Table 6.10** – Dissolved metals in selected world rivers measured by ultra clean techniques (from various sources collected by Cossa et al., 1993, 1996, except * which are from Zhang and Wollast (1993); () ultra clean stations doubtful.)*

	Cd (µg/l)	Cu (µg/l)	Hg (µg/l)	Ni (µg/l)*	Pb (µg/l)	Zn (µg/l)
			Impacted rivers - Europe			
Rhine	--	(4.5)	0.0040	2.0	(1.02)	(44.9)
Scheldt	--	--	0.0023	2.0	0.46	11.5
Seine	0.030	1.9	0.0028	--	--	--
			Impacted rivers - North America			
St Laurence	0.018	--	--	1.35	--	0.20
Mississippi	0.016	1.6	--	--	--	--
Hudson	0.225	2.5	--	--	--	--
			Non-impacted rivers			
Lena	0.005	0.6	0.0010	--	0.017	0.35
Ob	--	--	0.0005	--	--	--
Amazon	0.004	1.6	--	0.3	--	--

6.5 - Ecological risks and recent trends in the Po River

As we avoided in our study the use of the data collected by national monitoring agencies (see above), no time series of the evolution of heavy metal concentrations over several years are presented. But one example, which may be used for an assessment of the evolution during recent years, is the work of Camusso et al. (2000). They studied the heavy metal concentrations in the waters and sediments of the Po and the Rhine rivers over the period 1988-1995. This study is interesting because it allows both a spatial and temporal comparison of two major Mediterranean and north western European rivers, together with an evaluation of the environmental risk associated with the heavy metal concentrations.

When comparing the total metal concentrations (µg/l) in the Po and the Rhine waters for the years 1988, 1990, 1995 and 1996, Camusso et al. (2000) found major differences (2-3 fold) between these two periods for Cd in both rivers, for Zn, Cr and Hg in the Rhine, and for Pb in the Po (fig. 6.1). The evidence points to a real decrease in metal concentrations over the period 1988-1995 for the Rhine, whereas the strong reductions in the Cd and Pb levels in the Po over the same period could also be influenced by variations in the hydrological condition of the river.

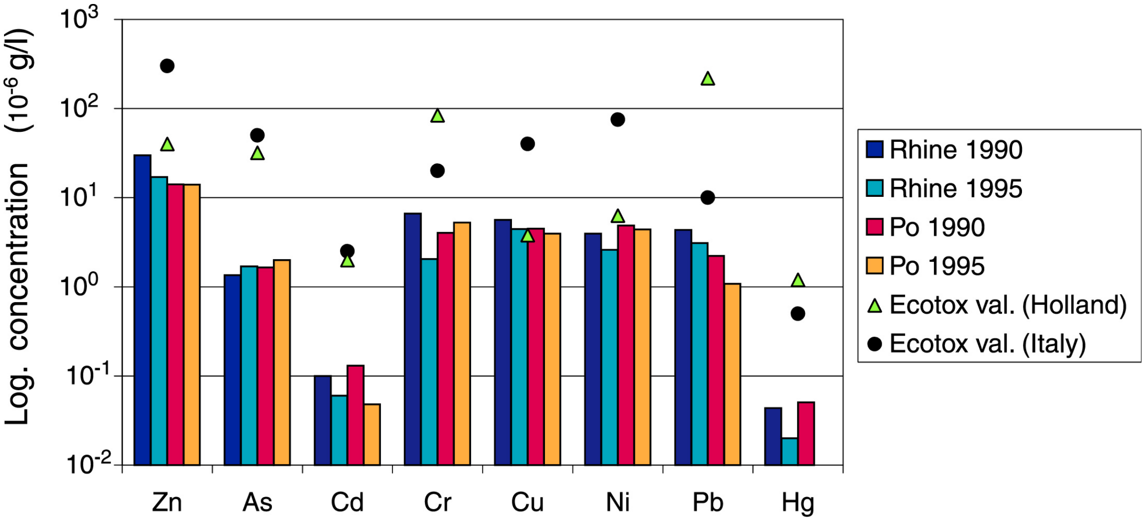

Fig. 6.1 – Comparison of total metal concentrations (µg/l) in the Rhine and Po waters at the stations of Lobith and Pontelagoscuro (stations close to the river mouths). The current Dutch and Italian water quality standards are also shown (figure from Camusso et al., 2000).

In 1995, none of the metals exceeded the current ecotoxicological quality criteria for the protection of aquatic life, with the exception of Cu, which remained slightly above the most stringent standard. These results suggest that the ecological risks from the present concentrations of trace metals in the water phase are minimal and limited to species that are particularly sensitive to Cu. However, it must be noted that only for As, Cd and Hg do the permitted levels adopted by the Dutch and the Italian water boards match closely; differences up to one order of magnitude exist for the other elements. Furthermore, except for Cd, Hg and Zn, the Italian criteria refer to the dissolved instead of total metal concentrations.

With respect to sediments, contamination by trace metals was found to be higher in the Rhine than the Po, especially in the Rhine delta where all Dutch ecotoxicological values, except that for Pb, were exceeded (fig. 6.2). In particular, Cu and Zn concentrations in this area were about 8 times higher than the proposed maximum, with levels for Ni, As, Cd, Cr and Hg 5, 3, 3, 2 and 1.5 times higher, respectively. At Lobith, metal concentrations were generally an order of magnitude lower than those in the Rhine delta, and only Cu, Ni and Zn levels approached, or slightly exceeded, permitted values. It seems therefore that Rhine sediments are still affected by the severe industrial pollution that entered the river in the 1970s and early 1980s, although the implementation of the Rhine Action Plan and subsequent recovery programmes have led to huge improvements in water quality. In the 1995 Po sediments, metal levels, except that for Ni, were not higher than the proposed ecological values. In the Po delta Cd, Ni and Pb concentrations were about 2 times higher than those at Pontelagoscuro, while no substantial differences were found for the other elements.

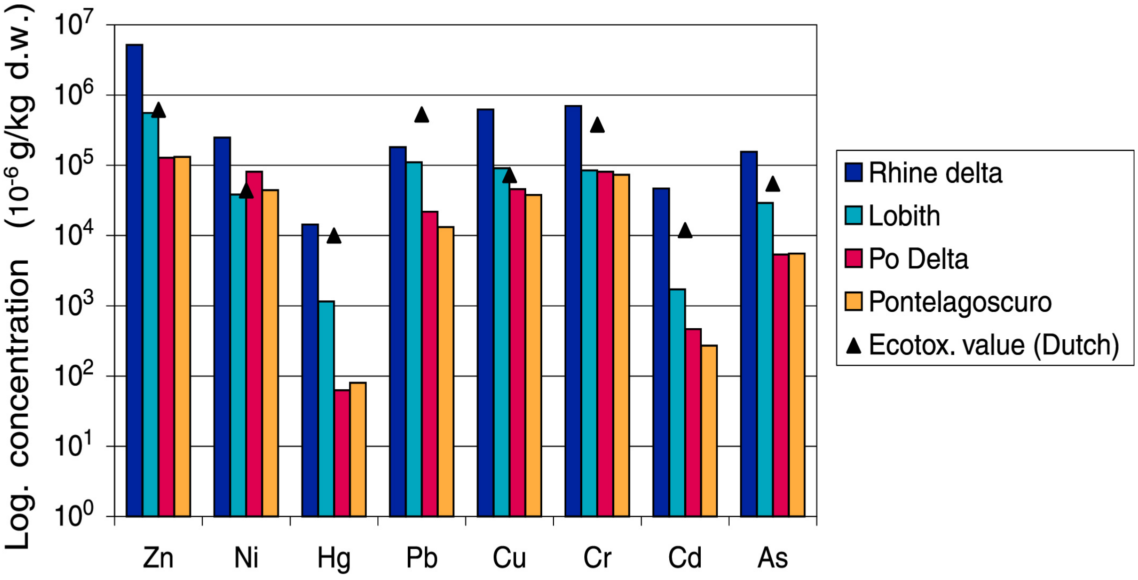

Fig. 6.2 – Trace metal concentrations (μg/g dry weight) in sediments from stations in the Rhine and Po rivers and their deltas (see text for details). The current Dutch sediment quality standards are also shown (figure from Camusso et al., 2000).

The presence of marked spatial variations in contamination along the Rhine is related to the construction, during the 1970s, of numerous dikes for flow regulation and flood prevention at the river mouth. These works increased the sedimentation of heavily polluted suspended material in the final stretches of the river. For the Po, evidence is accumulating that most sedimentation occurs in the pro-deltaic area facing the river mouth, where the levels of trace metals in sediments are 2 (Cd, Cr, Cu, Pb and Zn) to 7 (Hg) times higher than those at Pontelagoscuro.

Chapter VII - Pesticides and persistent organic chemicals

As for other pollutants, most rivers are not adequately monitored for persistent organic chemicals in order to assess loads, even though they are very important. High pesticide concentrations have been found in some specific studies and are believed to occur in many small rivers that are affected by intensive agriculture. The type of pesticides may vary from one river to another and from one country to another.

7.1 - Chlorinated pesticides

Cyclodiene pesticides (dieldrin, aldrin, endrin, heptachlor) have been reported in river water samples collected during the 1980s from Spain, Turkey, Slovenia, Egypt, Cyprus and Greece in a wide range of values (<0.1 – 228 ng/L, and even in the µg/L in some Turkish rivers) (Aya et al., 1997). Lower levels of these pesticides were observed in few recent studies. For example, 3.5-8.1 pg/L for heptachlor in the Nile River (Yamashita et al., 2000), 0.4-1.6 ng/L for total cyclodiene pesticides in the Ebro watercourse (Fernandez et al., 1999), 0.2-0-6 ng/L in the Rhone and Seine rivers (France) (Tronszynsky et al.,1996) and in only 2% of the samples from the major dams and rivers in Cyprus (max. 11 ng/L) (Michaelidou et al., unpubl.).

Surveys of DDTs have also been performed in several rivers, although only in France as part of a continued monitoring activity (Table 3.4). Extensive studies have also been performed in Egypt along the River Nile, with values ranging between 26 and 103 ng/L of total DDTs.

Table 7.1 - *Concentration of DDTs in freshwaters of the Mediterranean region*

Country	Location	Sampling	ΣDDTs conc. (ng/L)	References
Spain	Ebro River	1983-1987	pp'-DDE, 0.3-0.9 (d +p)*	Cid et al., 1990 & unpubl.
		1995 - 1996	3.1 ± 1.3 (d + p)	Fernandez et al., 1999
	Guadalquivir River		7 (d+p)	Hernandez et al., 1992
France	Rhone River	1995	pp'-DDE, 3.6 (d)	Tronszynsky et al.,1996
	Seine River	2000	pp'-DDT, 0.2-0.8 (d)	
Egypt	Nile River (Kafr El Zayat)		0.02-0.04	Dogheim et al., 1996
Cyprus	8 dams (84% of surface waters)	1996 - 2000	4 - 49	Michaelidou and Christodoulidou, unpubl.
	12 contributing rivers	1996 - 2000	0 – 4	

* p = particulate phase ; d = dissolved phase

Hexaclorocyclohexanes, and particularly lindane, have been identified in river waters. In France, lindane was detected, in a wide range of values (5-95 ng/L), in 23% of the river and estuarine water samples collected within the national monitoring network (Bintein and Devillers, 1996). More recently, the mean values found in the Rhone (n=34) and the Seine rivers have been of 5.6 and 7.0 ng/L, respectively (Tronszynsky and Moisan, 1996; Chevreuil et al., 1995).

In Spain, the values found in the Ebro River for α- and γ-HCH were in the range of 0.7-2.7 ng/L (d + p) (Fernandez et al., 1999), but values one order of magnitude higher were reported in certain sites of the Guadalquivir (54 ng/L) and Llobregat (10-30 ng/L) (Hernandez et al., 1992).

Relatively high concentrations of γ-HCH (39-360 ng/L) have been reported in water samples collected during the 1980s from the Nile River (El-Gindy et al., 1991). In a study carried out in 1993-1994 (Yamashita et al., 2000), levels decreased to the range 0.05-0.5 ng/L in the Nile River and Manzala Lake.

Hexaclorobenzene was found in water samples collected during the 1980s at the lower course of the Ebro River (Spain) with levels in the range 0.2-3 ng/L (Cid et al., 1990). Similar low levels (0.2-0.6 ng/L) were reported more recently in the Rhone (Arles, France) and the Seine River at Rouen (Tronszynsky and Moisan, 1996; Chevreuil et al., 1995). Lower concentrations were reported in 1993 for the Nile River (Egypt) and in the coastal Manzala lagoon (Yamashita et al., 2000).

7.2 - PCBs

Most studies were performed in the 80s, including urban waste and river waters, although the different units used preclude an accurate assessment of levels. Few measurements performed in the Ebro (Spain), Kupa (Slovenia) and Nile (Egypt) Rivers showed values (dissolved +particulate) in the range of 2-3, <1.5-5.0, and 17-653 ng/L of Aroclor 1254, respectively (Cid et al., 1990; Picer et al., 1995; El-Gendy et al., 1991). More recent studies are reported in Table 3.5. In this respect, a steady downward trend (by a factor of ten) has been found from 1989 to 2000 in Cyprus in the major dams and rivers of the island.

Table 7.2 - *Concentration of PCBs in fresh and wastewaters of the Mediterranean region*

Country	Location	Sampling	PCBs conc. (ng/L)	References
Spain	Ebro River	1983-87	76.3 ± 23.4	Fernandez et al., 1999
Egypt	Ismailia canal		Max.77	Badawy, 1997
	Mahmoudia canal		Max.39	Badawy, 1997
	Nile Delta	1995-97	570 -1000	Abassy et al., 1999
Cyprus	7 dams 12 rivers	1996-2000	Max: 60 (Σ14 cong) Max: 31 (Σ14 cong)	(Michaelidou and Christodoulidou, unpubl.)
Serbia and Montenegro	Danube River	1999	Median: 10.5 (Σ7 cong)	UNEP/UNCHS, 2000
	Lepenica River	1999	18.7 (Σ7 cong)	UNEP/UNCHS, 2000

7.3 - Coastal discharges

An analysis of general trends in concentrations of some pollutants over a decade reveals a marked stability in measured levels, with irregular tendencies to improvement and deterioration. Compared with the situation during the 1970's, progress in the reduction of sources of domestic and industrial pollution has, for example, reduced the impact of the Rhône. This should also be the case in the next few years for the Seine, the Ebro and the Po.

During MEDPOL Phase I (1975–1980), it was attempted through the project MED X to estimate the quantity and nature of riverine inputs in the region. The project met with considerable difficulties. Country responses were geographically almost restricted to the northern Mediterranean. Sampling frequency, sample pre-treatment, analytical methods and reporting formats varied widely. Some pollutants were rarely analysed (metals, specific organics, organochlorines). Field measurements of domestic sewage and industrial wastewater were very limited. No field measurements on agricultural run-off were available. Among 68 rivers registered, only 30 were adequately monitored, but not for PTS.

In view of the limitations and difficulties encountered, assessments of the pollution loads from all land based source (LBS) categories have been carried out, largely, by indirect computations and extrapolations. They have been worked out taking into account demographic statistics, the GNP of the countries, industrial production and manpower, and agricultural data. The time allowed for this ambitious project was too short for any in-depth study of each and all pollution sources in the Mediterranean. For this reason and for the fact that the results were pooled for each of ten UNEP Mediterranean regions, the project did not fulfil the requirements of its first objective, to provide the basis for national management and control plans.

Due to the difficulties and the uncertainties involved in the complex computations and extrapolations carried out, the results could not be better than rough estimates reliable within an error margin of one order of magnitude. Some of these results were proved, at a later stage, to be even worse. Only a comparative assessment of the regional contributions to the pollution load could be made. The results showed that the heaviest loads are discharged into the north western basin with one-third of the total pollution load. The Adriatic Sea receives about one-quarter of the total load. Moderate pollution loads are encountered in the Tyrrhenian and the Aegean Seas, as they receive each about 10% of the total load. The other six Mediterranean Sea areas each account for no more than 5% of the total.

More recently, accurate estimates have been obtained for some French rivers using linear regression and average weighted flow models. A survey was carried out during 1994-95 at the lower course of the Rhone River, far from the any marine influence. An important conclusion was that the large supply of fresh water (>70%) and consequently of dissolved species, corresponds to the medium-low flow regimes, whereas the contribution of large flows (>5000 m^3/s) represents less than 10% of the total input. On the contrary, these regimes contribute with about 80% of the total input of suspended particles. All pollutants, and notably PTS attached to the particles, are carried to the sea in such episodic events.

The calculation included dieldrin, endosulfan, heptachlor, HCB, □-HCH, □-HCH, pp'-DDE and PCBs (□7 congeners) and are reported in Table 6.10. The load of lindane was consistent with the use of this compound in the preceding years (1500 tons/year) but the DDE is reflecting the leaching of the existing environmental stock.

Table 7.3 - *PTS inputs (in kg/year) of the Rhone River into the Mediterranean (1994-95)*

	HCB	□-HCH	□-HCH	pp'-DDE	PCBs	Dieldrin
Dissolved	14	124	360	230	-	-
Particulate	157	23	21	51	304	33

Similar calculations performed in the Ebro River in early 90s gave values one order of magnitude lower, consistent with the difference in water input (see Table 4.5). In any case, the determination of river inputs requires an optimisation of the sampling strategy and statistical evaluation of data (modelling) due to the large variability of hydrologic regimes of the Mediterranean rivers.

As mentioned before, contaminated coastal sediments arise from freshwater discharges. However, beyond the zone of influence of these discharges, concentrations drop rapidly reflecting the enhanced sedimentation processes which take place at the freshwater-seawater interface. In fact, 80% of the terrestrial sediments are trapped on the continental shelf, and only the finest particles are transported by currents to deep-sea sediments. Indeed, atmospheric transport may be the main route by which pollutants enter the open sea basin.

7.4 - Temporal trends

Decreasing trends have generally been observed for persistent organochlorine insecticides (α-HCH, β-HCH, lindane, aldrin, dieldrin, heptachlor, and heptachlorepoxide, o,p'-DDE, p,p'-DDE, o,p'-DDT, and p,p'-DDT) in surface streams during the 80s and 90s (UNEP, 1999).

In the Nile River waters (Egypt), for example, levels decreased by 100-200 fold in the period 1982-1993. Although this difference can be partially attributed to the accuracy in the analytical methods, a certain decline exists, despite a limited use of DDT in the country.

Accurate trends have been obtained for several chlorinated pesticides in French rivers. Figure 7.1 shows the profiles exhibited by aldrin, DDT and lindane, from 1978 to 2000 in the Seine River. The temporal trend clearly reflects the pattern of use of these compounds in the country.

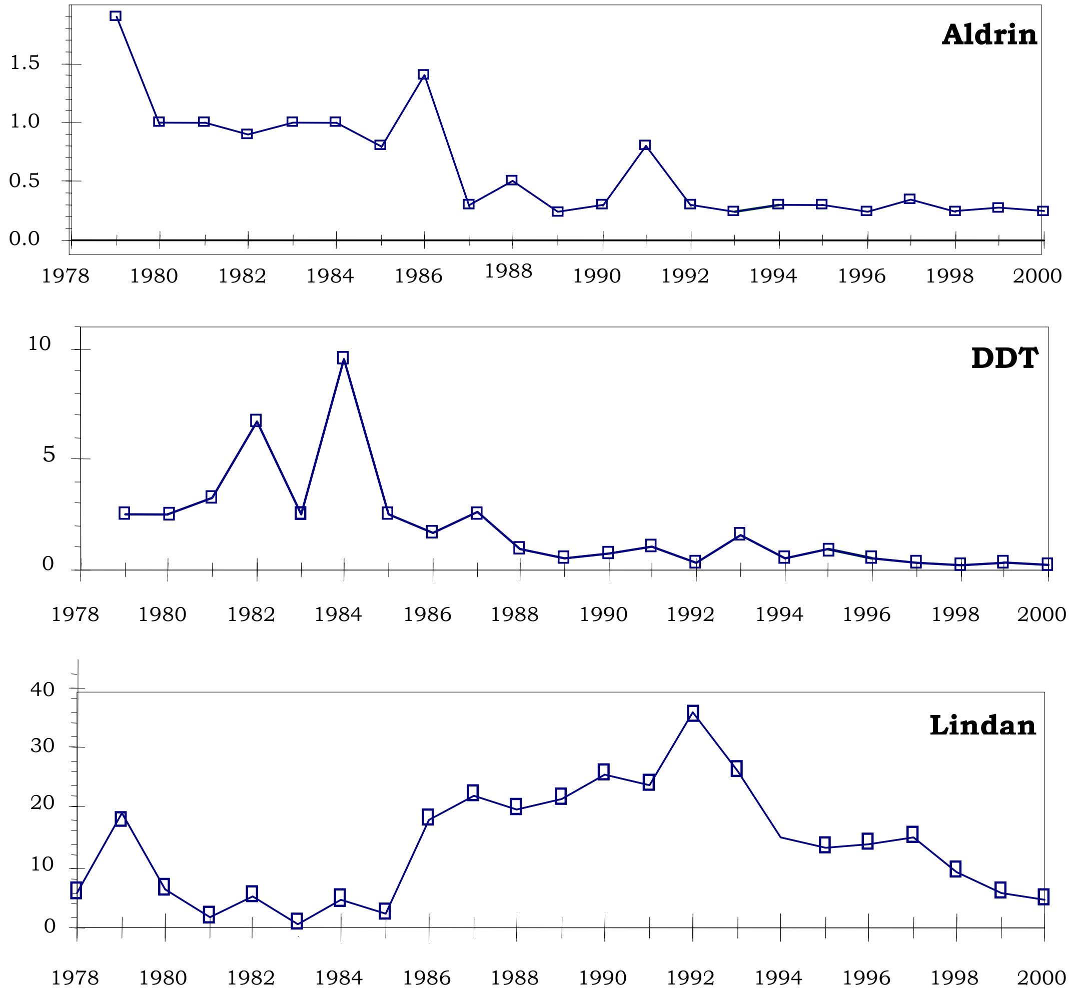

***Figure 7.1** - Temporal trends of concentrations (in ng/L) of some pesticides in the Seine River*

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