THE ROLE OF ATMOSPHERIC DEPOSITION IN THE BIOGEOCHEMISTRY OF THE MEDITERRANEAN SEA

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Abstract

Estimates of atmospheric inputs to the Mediterranean (MED) and some coastal areas are reviewed, and uncertainities in these estimates considered. Both the magnitude and the mineralogical composition of atmospheric dust inputs indicate that eolian deposition is an important (50%) or prevailing (>80%) contribution to sediments in the offshore waters of the entire

Mediterranean (MED) basin. Model data for trace metals and nutrients indicate that the atmosphere delivers more than half the lead and nitrogen, one-third of total phosphorus, and 10% of the zinc entering the entire basin. Measured data in sub-basins, such as the north-western MED and northern Adriatic indicate an even greater proportion of atmospheric versus riverine inputs. When dissolved fluxes are compared (the form most likely to impinge on surface water biogeochemical cycles), the atmosphere is found to be 5 to 50 times more important than rivers for dissolved Zn and 15 to 30 times more important for Pb fluxes. Neglecting co-limitation by other nutrients, new production supported by atmospheric nitrogen deposition ranges from 2-4 g C m^{-2} yr^{-1}, whereas atmospheric phosphorus deposition appears to support less than 1 g C m^{-2} yr^{-1}. In spite of the apparently small contribution of atmospheric deposition to overall production in the basin it has been suggested that certain episodes of phytoplankton blooms are triggered by atmospheric deposition of N, P or Fe. Future studies are needed to clarify the extent and causal links between these episodic blooms and atmospheric/oceanographic forcing functions. A scientific program aimed at elucidating the possible biogeochemical effects of Saharan outbreaks in the MED through direct sampling of the ocean and atmosphere before and after such events is therefore highly recommended.

Introduction

Over the past two decades it has become apparent that the atmosphere is not only a significant but in some cases the dominant pathway by which both natural and pollutant materials are transported from continents to both coastal and open seas. These substances include mineral dust, plant residues, heavy metals, nitrogen species from combustion processes and fertilisers, pesticides, and a wide range of synthetic organic compounds from industrial and domestic sources. Some of these substances, such as lead and some chlorinated hydrocarbons, when carried into oceans by the atmosphere, are potentially harmful to marine biological systems. Others, such as nitrogen species, phosphorus and iron, are nutrients and may enhance marine productivity. For some substances (e.g. aluminium, cadmium, lead, and some rare earth elements), atmospheric flux has an important impact on their oceanic chemical cycles. Atmospheric inputs may thus exert many different effects on the marine environment, and it is necessary to understand the magnitude and geographical distribution of the atmospheric fluxes of these materials to both coastal and open seas. Indeed, there have recently been a number of intensive studies of atmospheric inputs to coastal waters in North America and Europe, with several studies also devoted to investigating these processes in open oceans.

The most complete review of this subject, updated to the early 1990s, was a report by the Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP, 1989), much of which was subsequently published as a review article in the scientific literature (DUCE *et al.,* 1991). The present paper briefly reviews results from several of these studies, especially those related to the Mediterranean Sea.

The biogeochemical effects of mineral dust deposition to the water surface are of interest from several perspectives. The observation of more than 30-fold increases in dust deposition during glacial periods suggests a link between climatic oscillations and carbon cycling in the surface ocean on global and glacial scales (MARTIN, 1990). This link is created through the roles played by eolian deposition in supplying Fe to remote parts of the open ocean and by iron limitation in controlling primary production. In these high-nutrient/low-chlorophyll (HNLC) regions, there may be a direct connection between atmospheric and biological processes (MARTIN, 1990; KUMAR *et al.,* 1995).

Dust input to the nutrient-limited Mediterranean (MED) basin (2.3×10^6 km^2) is one of the greatest in the contemporary ocean (20-50 x 10^6 tons yr^{-1}) and it is thus a natural laboratory in which to study the effects of dust deposition on the surface ocean in a setting that is distinct from the HNLC regions (COALE *et al.,* 1996). There have been several hypotheses suggesting that this large dust input is responsible for biogeochemical effects, although no concerted scientific program aimed at elucidating these effects directly has yet been set up.

The aim of the present paper is to review current understanding of the magnitude and effects of dust inputs to the MED and to highlight important areas of uncertainty. Section 1 considers the magnitude of atmospheric dust inputs and problems related to their estimates. Section 2 compares fluxes of trace elements from atmospheric and riverine sources and considers evidence that atmospheric inputs affect the chemistry of surface waters in the MED. Section 3 looks at the role played by atmospheric processes in delivering nutrients to the surface MED and their spatial effects. Section 4 considers current hypotheses of mechanisms by which atmospheric deposition is believed to affect surface water biogeochemical cycles, focusing particularly on the roles of phosphate and iron, and reviews what evidence exists to evaluate them.

1. Magnitude and mineralogical composition of atmospheric mineral dust input

Budgets and residence time estimates for trace metals and nutrients in the oceans have traditionally been based on riverine fluxes and have neglected atmospheric and other inputs. For most major and minor components of seawater, the atmosphere has generally been assumed to be a secondary source. However, over the last 20 years systematic studies of atmospheric inputs to the MED have been undertaken, and sufficient data are now available to allow fairly reliable estimates to be made. The most comprehensive study is that prepared by GESAMP (1989), together with several recent reviews devoted to the Western MED within the EROS 2000 project (MILLIMAN and MARTIN, 1997).

For rivers, there is the major problem of understanding and quantifying transport through estuarine and coastal regions to deep waters. MILLIMAN *et al.* (1995) and GESAMP (1989) both attempted to address this problem by compiling run-off data for countries surrounding the MED. It is important to note, however, that many of these data reflect historic not present-day discharges. A good example of this is the decreased flow to the western MED, as illustrated in the introduction to the EROS-2000 DSR-II special issue (MILLIMAN and MARTIN, 1997). The Rhone and many Italian rivers currently have discharges very similar to those of 40 years ago, whereas most Spanish and north African rivers have been dammed in the past 20-30 years.

Atmospheric flux estimates suffer from an undersampling problem. The atmosphere is a very dynamic compartment of the earth's system, within which concentrations of reactive gases and particulate matter vary considerably in space and time. This variability ranges from rapid day-to-day changes in pollutant concentrations (lead, cadmium, NOx, SOx) to massive temporal and spatial changes in dust

loading over the entire MED (Tab. 1.1), as a result of dust storms in North Africa (GUERZONI *et al.,* 1997; BERGAMETTI, 1989; DULAC *et al.,* 1989, 1996; LOŸE-PILOT and MARTIN, 1996).

Tab. 1.1 - Range of insoluble particulate load concentrations in air and rain during two years at Sardinia (39°N, 9°E: from Guerzoni *et al.*, 1997).

	air (μg m^{-3})	rain (mg l^{-1})
Background	1-3	0.1-10
Desert-enriched	20	10-50
Saharan outbreaks	44	50-500
Maximum recorded	110	510

background :Al/Si < 0.3; Ca <2 %; associated rain pH < 5.60; Ca < 200 meq l^{-1}
desert enriched = Al/Si > 0.3; Ca > 2 %; Saharan outbreaks = Al > 1000 ng m^{-3}; Al/Si > 0.4; Ca > 4%.

The high spatial and temporal variability of dust transport and deposition, coupled with the short duration of oceanographic research cruises, has made it difficult to obtain good estimates of dust deposition to those areas of the open ocean devoid of islands at which continuous sampling can be undertaken.

Encouragingly, however, recent results from ship-board collections of aerosol metals over the North Sea, where a steep spatial gradient in aerosol concentration is found (YAAQUB *et al.,* 1991), are comparable to samples collected at the coast (CHESTER *et al.,* 1993; KANE *et al.,* 1994). This finding suggests that atmospheric fluxes estimated from coastal sites may be extrapolated to adjacent marine areas. A similar result was found in the Western MED (WMED) where MARTIN *et al. (*1989) and CHESTER *et al. (*1993) showed that background aerosols at sea have similar Pb and Cd values to those collected at a remote coastal station in Sardinia (GUERZONI *et al.,* 1997).

Despite the shortcomings of these estimates, for many trace elements (e.g., Al, Pb, Zn), it has been shown that the local dissolved flux from partial dissolution of eolian dust in surface waters is much greater than that carried by the Rhone and Po rivers into the WMED and Adriatic respectively (GUIEU *et al.,* 1997; GUERZONI *et al.,* in press). Even where river fluxes appear to be similar in magnitude to those of dust, estuarine and near-shore removal processes attenuate river fluxes severely, often resulting in little of the riverine signal penetrating into offshore regions. An exception to this is Cd, which forms stable and soluble complexes with chlorides and may also be desorbed from river-borne particulate during estuarine mixing, so that in this case the input very often influences open basin waters (BOYLE *et al.,* 1985; Elbaz-Poulichet *et al.,* 1989).

1.1. Atmospheric mineral particle fluxes and mineralogy

Beside the undersampling problem, several theoretical problems also hinder our ability to derive atmospheric flux estimates to the ocean from atmospheric suspended loads. It is therefore useful to compare the measured data with the results of GESAMP flux calculations (DUCE, 1991).

Fig. 1.1 and Tab. 1.2 list most of the coastal stations where long (2-11 yrs) time series data are available together with an inventory of mean annual bulk dust fluxes around the Mediterranean. Flux values are deduced from a combination of aerosol suspended loads, dry, wet and bulk deposition samples. Sampling frequency at the various sites ranged from a few days (aerosols) to a few weeks (bulk).

Mean annual deposition mass fluxes of mineral dust for the WMED range from 3-12 g m^{-2} yr^{-1}, whereas much higher values are found (20-50 g m^{-2} yr^{-1}) in the Eastern MED (EMED). The measured data are higher than those calculated with the GESAMP model using precipitation rates and a scavenging ratio (SR) of 200. As the SR for the MED is probably higher (GUERZONI *et al.,* 1996), mass fluxes were recalculated using an SR of 500, and are listed in Tab. 1.2. When SR=500 is used, the two estimates agree very well.

With the data from table 1.2 we can calculate mean values of 8, 12 and 35 g m^{-2} yr^{-1} for WMED, CMED and EMED respectively, and use these values to estimate the total annual atmospheric dust flux, which turned out to be ~40 x 10^6 tons for the whole Mediterranean basin (Tab. 1.3). This estimate may be compared to total riverine discharge estimates recently revised by LOICZ (MILLIMAN *et al.,* 1995). The sub-areas indicated by GESAMP (Nos. 1 to 10, shown in Fig. 1.1) were used for calculations.
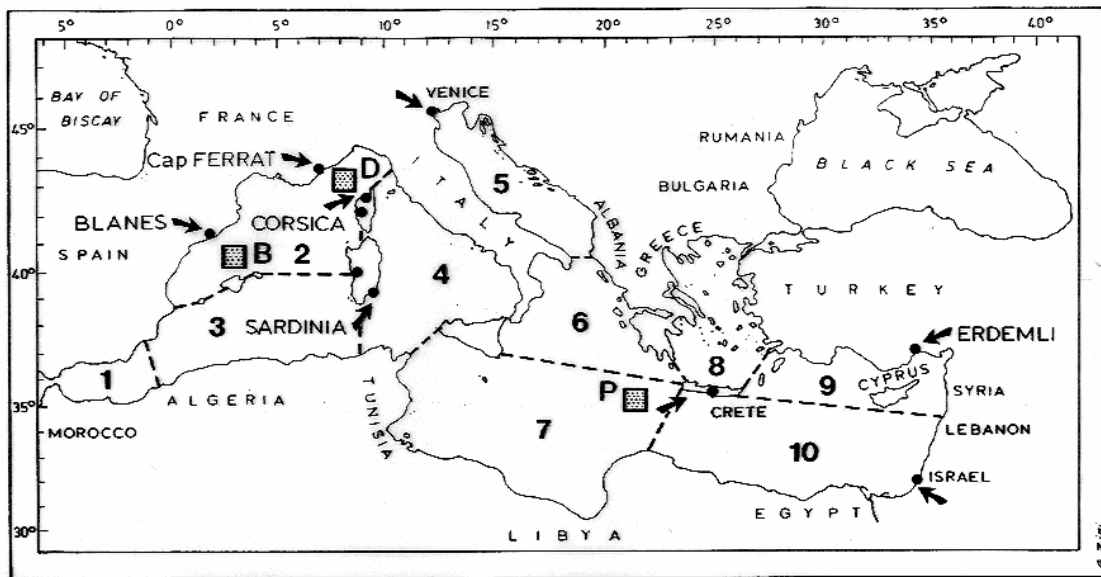

Fig. 1.1 - Arrows indicate the location of sampling sites for which time series of atmospheric data are available. Squares: sediment trap locations (B=Balear; D=Dyfamed; P=Paleoflux). Division in sub-areas 1-10 according to UNEP (1984) for budget calculations.

Tab. 1.2 - Mean annual (and range) atmospheric mass fluxes (g m^{-2}) measured at various coastal sites (refer to Fig.1.1 for site locations). Mean fluxes for three sub-basins calculated by averaging Spain, SE France, Sardinia and Corsica for WMED, Corsica, NE Italy and Crete for CMED, and Crete and Israel for EMED. Estimates from GESAMP model (DUCE, 1991) calculated with scavenging ratio values of 200 and 500 respectively.

site	flux g m^{-2}	sub-basin	mean g m^{-2}	GESAMP SR=200(500)
Spain[a]	5(1-11)			
SE France[b]	4 (2-11)			
Sardinia[c]	8 (2-12)	WMED	8	3.4 (8)
Corsica[d]	12 (4-25)			
NE Italy[e]	3 (2-6)	CMED	12	7(18)
Crete[f]	21 (6-46)			
Israel[g]	50 (36-72)	EMED	35	14 (35)

(a) CARRATALA *et al.* (1996); RODA *et al.* (1993); (b) GUEIU *et al.* (1997); (c) GUERZONI *et al.* (1997); LE BOLLOCH and GUERZONI (1995); (d) LOŸE-PILOT *et al.* (1996); BERGAMETTI *et al.* (1989); (e) GUERZONI *et al.* (in press); ROSSINI and GUERZONI (1996); (f) NIHLEN and MATTSSON (1989); PYE (1992); (g) HERUT and KROM (1996).

Table 1.3 - Comparison of riverine discharge (R) and atmospheric (A) input of insoluble particles to Mediterranean Sea. Data on riverine discharge are from MILLIMAN *et al.* (1995). Atmospheric mass inputs derived from average fluxes in three sub-basins (west to east) of 8-12-35 g m^{-2} yr^{-1}, respectively (see Tab. 1.2 and text for explanation).

Sub-basin	Area (10^{6}km^2)	mass (10^{6}tons)		
		R	A	%A
WMED	0.84	30	7	19
CMED	0.80	35	10	22
EMED	0.70	10	24	70
Total	**2.34**	**75***	**41**	**35**

(*) if 2/3 of riverine input remains on the continental shelf (< 100 m) then the offshore riverine discharge is reduced to 25 x 10^6 tons, and the atmospheric contribution increases to ~60%.

1.1.1. Mineralogy

LOŸE-PILOT *et al. (*1986) and GUERZONI *et al. (*1997) have shown the relationship between eolian deposition and deep sea sedimentation, and found that the atmosphere contributes on average from 10 to 30% of recent sediments. Here, we highlight differences among sub-basins and the possible role of mineralogy in identifying the sites where the atmospheric input is most important.

The mineralogical signature may be used as an indicator of dust origin. Mineral dust mainly consists of a mixture of silicates (clay minerals, feldspar, quartz) associated with carbonates. The abundance of each of these minerals in dust is highly variable, mainly reflecting the source composition and its

evolution during transport. Several studies have examined specific minerals within the clay to identify source regions. For example, palygorskite has been used as an indicator of dusts of north-west African origin in samples collected over the MED (TOMADIN and LENAZ, 1989; MOLINAROLI and IBBA, 1995; MOLINAROLI, 1996).

Another approach is to look for mineral associations which are characteristic of dust sources. For example, illite is an ubiquitous clay and is not characteristic of any particular weathering regime, whereas kaolinite, which may also be produced in a variety of weathering conditions, is characteristic of desert weathering regimes. A comparison of the mineralogy of dusts collected throughout the MED shows that illite reaches its highest value in the CMED and its lowest in the EMED (Tab.1.4). In the CMED mixed dusts are observed. Kaolinite is more abundant in dust originating from the eastern compared to western Sahara, the highest concentrations being observed off the Egyptian coast. Smectite is very common in the EMED but not in the WMED. A comparison between dust and sediment has been attempted (CAQUINEAU *et al.,* in press) by considering the difference between illite and kaolinite distributions in the Mediterranean and the illite/kaolinite ratio in the African source dust. The comparison between the I/K ratio in dust and sediments is shown in Tab 1.4. WMED dust transported from the Sahara originating from north-west Africa shows an I/K ratio of 1.8. CAQUINEAU *et al. (*in press) observed a range of I/K values from 2.4 to 1.6 in north-west Africa. The similarity of the I/K ratio between dust and sediment (I/K=1.8) in the WMED indicates that the major contribution to sedimentation in this region is from dust deposition from the western Sahara. This conclusion contradicts data from Table 1.3, which indicates an overwhelming river contribution in this region. The fact that the sediment I/K ratio appears to be set by atmospheric dust probably indicates that a large fraction of the riverborne material is deposited on shelves.

Tab. 1.4 - Average of clay mineral compositions and I/K ratio in Saharan dusts (D) and sediments (S) in MED basin.

Sample	Illite	Chlorite	Kaolinite	Smectite	I/K
WMED (D)	53	9	29	9	1.8
WMED (S)	48	10	26	16	1.8
CMED (D)	66	12	16	3	4.0
CMED (S)	45	12	13	30	3.5
EMED (D)	32	5	38	25	0.8
EMED (S)	15	5	35	45	0.4

This average was compiled using data from several authors:
CHESTER *et al.* (1984) (3 samples); MAZZUCCOTELLI *et al.* (1986) (3 samples); MOLINAROLI (1996) (10 samples) for the WMED.
LENAZ *et al.* (1988) (5 samples) for the CMED.
CHESTER *et al.* (1977) (7 samples) GANOR and FONER (1996); (17 samples); TOMADIN and LENAZ (1989) (3 samples) for the south-EMED
TOMADIN (1981) (3 samples) for the (S) WMED
TOMADIN and BORGHINI (1987) (4 samples) for the (S) CMED
VENKATARATHNAM and RYAN (1971) (20 samples) for the(S) EMED

The CMED has an average I/K ratio of 4.0 in dust and 3.5 in sediments. This very high ratio shows that the dust is a mixture of Saharan and background dusts (European), since CAQUINEAU *et al. (*in press) demonstrated that the I/K ratio is always <2.4 in African regions.

The EMED has a low I/K ratio (0.8) in dust and 0.4 in sediments. A relatively low I/K ratio (0.7) is associated with north east African sources by CAQUINEAU *et al. (*in press). The similarity between dust and sediment values again indicates that the major contribution to sedimentation is from dust deposition, in particular from the eastern Sahara.

<u>1.2. Sediment trap estimates</u>

Many sediment trap studies have been or are being carried out in the MED, e.g. Mediterranean Targeted Projects 1 and 2 (MTP1 and MTP2), but very few of these are useful for studying dust deposition, mainly because of their location relative to river inputs.

For instance, among the traps in the WMED, very different results have been derived from those deployed in the Balearic basin (39°N, 3°E; "B" in F ig. 1.1) with mass fluxes of 50-70 g m^{-2} yr^{-1}, compared to the DYFAMED site (43°N, 8°E; "D" in Fig . 1.1) where average fluxes are 31-35 g m^{-2} yr^{-1}. In addition, the relative contribution of the lithogenic fraction is different between the two sites (60% and 25%, respectively). The high flux and lithogenic contribution to the Balearic site is probably related to bottom resuspension and coastal run-off.

The trap used in Paleoflux, MARFLUX (34°N, 20°E; ZI VERI *et al.,* 1996; "P" in Fig. 1.1) is in the best location for dust flux measurement in the EMED, since river discharge is negligible in this region. The total annual average flux recorded in this 3000m deep trap deployed between November 1991 and August 1994, was around 25 g m^{-2} yr^{-1}, with approximately 60% of lithogenic origin (RUTTEN *et al.,* in press; ZIVERI *et al.,* submitted).

HEUSSNER and MONACO *(*1996) showed that two flux gradients of total mass are evident in the MED, and that they are related to trophic conditions. A gradient of decreasing flux is seen on the scale of the entire MED basin from west to east, roughly corresponding to the degree of oligotrophy. Within each sub-basin, a second gradient of trophic conditions appears, of decreasing flux from north to south. The inorganic carbon flux is observed to be slightly higher in the EMED, perhaps related to desert-derived carbonate inputs. The above authors conclude that seasonal variations in fluxes in the traps are essentially due to changes in continental input rates to the MED system, i.e., direct deposition of dust through rain and the effect of rain-induced river run-off (HEUSSNER and MONACO*,* 1996). The sensitivity of traps to river run-off explains why few of these sites can be used for absolute and relative quantification of Saharan dust export flux to the MED. In fact, as far as we are aware, it has been difficult (if not impossible) to distinguish between lithogenic material from dust and that from river discharge in trap samples.

Despite these problems, trap data from the DYFAMED (WMED) and Paleoflux (EMED) sites appear to be promising. At both sites, the lithogenic flux appears to be similar to or smaller than the eolian fluxes

estimated for the region from coastal sites (Tab. 1.2). It is very important that, in future trap work, wherever possible, sites that are suitable for the task of quantifying dust deposition are chosen. The EMED is a particularly important region that needs more coverage of eolian deposition from sediment traps.

<u>1.3. Remote sensing and modelling</u>

In a series of recent papers, DULAC *et al. (*1996) and MOULIN *et al. (*1997a), presented an analysis of historical Meteosat data, which monitored dust export from Africa over the Mediterranean on a quasi-daily basis between June 1983 and December 1994. These authors showed that, despite large daily variability, there were clear seasonal cycles with minima during the dry season (November, December and January). The general pattern is that dust transport begins over the eastern basin in spring and spreads over the western basin in summer.

Tentative estimates of deposition fluxes were made from Meteosat vertically integrated dust concentrations, using simple deposition velocity approaches, on a yearly time scale at the DYFAMED station, and for shorter periods in the western basin (DULAC *et al.,* 1996). A similar paper was published with results for the DYFAMED station in the Ligurian Sea (MOULIN *et al.,* 1997b).The former authors compared Meteosat data with measured aerosols at the Corsica site for a six-month period (1/2/87-31/8/87) and found the average measured flux was 0.024 g m^{-2} day^{-1} (equivalent to approximately 9 g m^{-2} yr^{-1}), whereas Meteosat data yielded a flux of 0.01-0.03 g m^{-2} day^{-1} (4-11 g m^{-2} yr^{-1}) for the same period.

DULAC *et al.* (1996) also compared Meteosat-derived atmospheric fluxes in 1987 and 1988 with seawater dust fluxes measured in sediment traps at 200 m water depth during the same period at the DYFAMED station. If the periods with sediment trap data are examined, there are results for 364 days over a 2-year period. Seasonal variations are shown in Fig. 1.2. The minimum and maximum Meteosat-derived fluxes bracket the trap fluxes in summer and autumn 1987 and again between spring and autumn 1988. In both winters (1987 and 1988) the trap flux is greater than the maximum Meteosat estimates.

The Meteosat estimates show a similar range for both years (3.5-10.8 and 3.6-11.0 g m^{-2} yr^{-1}) while the sediment trap data show distinctly different fluxes (12 and 9 g m^{-2} yr^{-1}) in the two years. Some of this variability may be due to various short-term hydrological and biological processes that control the downward transport of particulate material in the water column. The susceptibility of trap data to short-term variations is shown in Fig 1.3, showing contemporaneous trap fluxes and Meteosat estimates.

2. Magnitude and fate of atmospheric trace metal inputs

<u>2.1. Trace metal concentrations in air</u>

Aerosols transported to the MED may be considered to consist of anthropogenic-rich "background" materials supplied continuously from Europe, upon which sporadic pulses of Saharan crust-rich dust
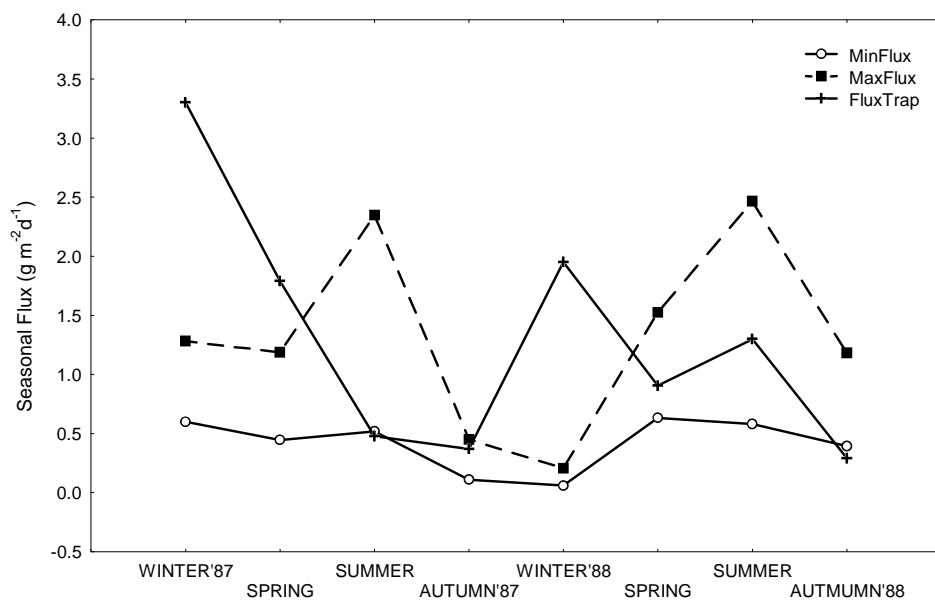
Fig. 1.2 - Seasonal Meteosat-derived (min/max) and sediment trap terrigenous fluxes at Dyfamed station, 1987-1988.
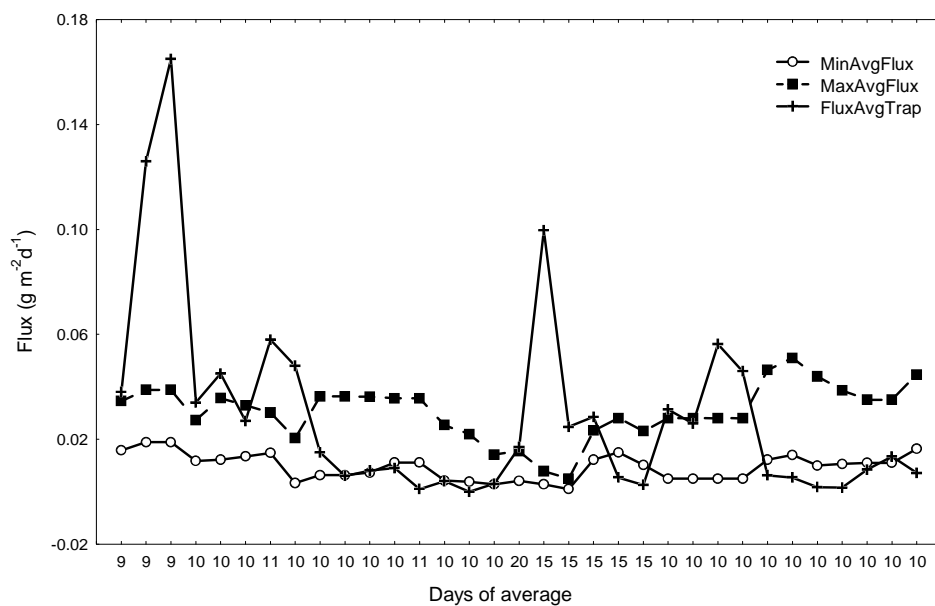

Fig. 1.3 - Time variations (seasonal scale as above) of Meteosat-derived and trap terrigenous fluxes (number of days is integration time of traps).

are superimposed. These two "end-member" aerosols have strikingly different trace metal composition, and this is clear in samples collected on board as well as at coastal stations (see Tab. 2.1).

Tab. 2.1 - Mean trace metal concentrations (conc. units: ng m^{-3} of air) and EF$_{crust}$ values for European anthropogenic-dominated and Saharan crust-dominated particulate aerosol populations collected over Tyrrhenian Sea (n=9, CHESTER *et al.*,1984) and at Sardinia (n=55, GUERZONI *et al.*, in press).

	European anthropogenic-dominated aerosol population (n = 5+48)		Saharan crust-dominated aerosol population (n = 4+7)	
	Concentration ship-Sardinia	EF$_{crust}$ ship-Sardinia	Concentration ship-Sardinia	EF$_{crust}$ ship-Sardinia
Al	112-210	1.0-1.0	2000-2929	1.0-1.0
Fe	117-84	1.7-8.3	1249-1139	0.9-1.7
Mn	4.3-5.4	3.5-1.5	19-24	0.8-1.1
Cr	1.0-0.5	8.6-3.3	4.9-3.3	2.9-1.1
Ni	1.3-5.3	15-21	3.1-7.3	2.8-4.1
Zn	12-22	120-63	8-28	6-18
Pb	1112	767-550	7-25	46-66
Cd	0.44-017	1219-80	0.31-0.08	96-12

Many studies have documented the airborne concentrations of trace metals over the Mediterranean Sea (DULAC *et al.,* 1987; GUERZONI *et al.,* 1988; BERGAMETTI *et al.,* 1989; CHESTER *et al.,* 1990, 1993; MIGON and CACCIA, 1990; MATEU *et al.,* 1993; MIGON *et al.,* 1993; Sandroni and Migon, 1997). Most metals have a relatively short residence time in the troposphere (between a few days and a few weeks; BERGAMETTI, 1987; BUAT-MÉNARD, 1993). They are not well mixed in the atmosphere and thus aerosols and rainwater are expected to exhibit strong spatial and temporal variability (BUAT-MÉNARD, 1993). However, while seasonal variability is observed in the NW Mediterranean (NICOLAS *et al.,* 1995), spatial variability is rather low for metals such as Al, Cd, Cu, Fe, Pb and Zn, and the annual averages from 7 coastal sampling sites are within the same order of magnitude (Tab. 2.2). (CHESTER *et al.,* 1990, 1993; GUIEU *et al.,* 1997; GUERZONI *et al.,* 1996; SANDRONI and MIGON, 1997).

Tab. 2.2 - Average trace metal concentrations and EF$_{crust}$ values for particulate aerosols from a number of Mediterranean Sea sites (conc. units: ng m^{-3} of air)

	Spain[1]		Corsica[2]		Sardinia[3]		Erdemli[4]		Cap Ferrat[5]		Vignola[6]	
	Conc.	EF$_{crust}$	Conc.	EF$_{crust}$	Conc.	EF$_{crust}$	Conc.	EF$_{crust}$	Conc.	EF$_{crust}$	Conc.	EF$_{crust}$
Al	398	1	168	1	480	1	680	1	370	1	109	1
Fe	316	1.3	144	1.25	278	0.85	685	1.5	320	1.3	-	-
Mn	10	2.2	4.3	2.7	7.4	1.3	12.6	1.6	11	262	1.7	1.4
Cr	1.8	3.4	-	-	0.51	0.89	10.8	13	2.5	5.6	-	-
Cu	7.9	29	2.1	18	-	-	-	-	6.2	24	1.9	26
Zn	50	148	l9	133	21	52	19	33	41	130	12	130
Pb	50	837	16	635	14	194	30	294	58	1045	9	550
Cd	0.60	628	0.66	1633	0.30	260	0.19	116	0.60	676	0.11	423

(1) CHESTER *et al.* (1993); (2) BERGAMETTI *et al.* (1989); (3) KEYSE (1995), GUERZONI *et al.* (1996); (4) KUBILAY and SAYDAM (1995); (5) CHESTER *et al.* (1990); (6) MIGON *et al.* (1993)

2.2 Metal fluxes (total, dry, wet)

Several authors who have attempted to estimate the atmospheric fluxes of metals to the surface ocean (CHESTER *et al.,* 1989; DULAC *et al.,* 1989; GUIEU *et al.,* 1991; MIGON *et al.,* 1991;

GUERZONI *et al.*, 1993; NICOLAS *et al.,* 1995; MIGON *et al.,* 1997) have pointed out the difficulties encountered in quantifying the different modes of atmospheric inputs, i.e. wet/dry/total and dissolved/particulate. While evaluation of wet inputs, calculated from rainwater concentration and rainfall amount, is generally reliable, that of dry deposition is more problematic. It has been calculated by a number of methods: i) on the basis of experimental cascade impactor data (e.g., BERGAMETTI, 1987; REMOUDAKI, 1990); ii) from theoretical models (e.g., DULAC *et al.,* 1989); and iii) with surrogate surfaces (e.g., DOLSKE and GATZ, 1985; BAEYENS *et al.,* 1990; GUIEU, 1991). Results differ greatly according to methodology. Comparisons between estimates must be interpreted with caution, principally as a result of poor knowledge of elemental mass-size distributions (DULAC *et al.,* 1989; MIGON *et al.,* 1991; BUAT-MÉNARD, 1993). For example, in the NW Mediterranean, DULAC *et al. (*1989) proposed a theoretical dry deposition rate of 0.04 cm s^{-1} for Pb, while REMOUDAKI (1990) gave an experimental value of 1.9 cm s^{-1}. Dry deposition rates are not well known for submicrometer particles (SLINN, 1983; ARIMOTO and DUCE, 1986), and difficulties increase when particle size exceeds 10 μm: in this case, deposition rates are very high and their estimation becomes very questionable (DUCE *et al.,* 1991). Moreover, phenomena such as fog or dew, which are common in coastal areas, significantly enlarge particles, thereby increasing their deposition rate (BERGAMETTI, 1987). Despite these problems, there is a significant amount of data on trace metal atmospheric fluxes, mainly for the Western and Central MED. They are listed in Tab. 2.3, which shows that the range of fluxes is quite high for some metals (e.g., Al, Cd, Zn), and lower for others (Cu, Pb, Fe, Ni) (GUIEU *et al.,* 1997; GUERZONI *et al.,* in press).

Tab. 2.3 - Range of total atmospheric fluxes (insoluble and soluble fractions), calculated from wet and dry deposition. 1=GUERZONI *et al.* (in press); 2=GUIEU *et al.* (1997).

μmoles m^{-2} yr^{-1}	CMED[1]		NWMED[2]	
	insoluble	soluble	insoluble	soluble
Al	11250-33000	330-890	4900-31500	370-3780
Cd	0.1-0.3	0.5-2.8	0.9-3.6	1.8-8.0
Cu	50-70	45-72	22-30	12-20
Fe	2600-7300	90-180	12500-14500	570-2500
Ni	8-32	17-24	7-9	7-9
Pb	5-38	5-24	6-11	4-9
Zn	46-76	210-460	15-1000	15-1150

2.3 Fate of trace metals in seawater

The magnitude of air-to-sea fluxes of trace metals partly depends on their concentrations in the air. However, the fate of an atmospherically-transported trace metal, once deposited at the sea surface, depends on its thermodynamic speciation in seawater, its speciation in the parent aerosol, and the kinetics controlling any speciation change. Aerosol speciation may be assessed by determining the partitioning of trace metals between the following fractions: (i) exchangeable, the most mobile, (ii) oxide/carbonate, intermediate mobility, and (iii) refractory, the least mobile. The speciation of trace

metals in aerosols is a function of the source of the aerosol since some trace metals have very different speciation signatures in anthropogenic-rich and crust-rich "end-member" MED aerosols (CHESTER *et al.,* 1996), and chemical changes occur during passage and transformation in the atmosphere prior to deposition on the sea surface.

Al and Fe are generally refractory in both end-member aerosols, Mn is speciated between all three fractions in both end-member aerosols, but Cu, Zn and Pb switch speciation signatures between the two end-member aerosols, being essentially refractory in crustal aerosols and exchangeable (i.e., mobile) in anthropogenic ones. Aerosols are removed from the air by dry fall-out and wet precipitation scavenging deposition modes.

In the dry mode, aerosols reach the sea surface directly and trace metal solubility is constrained by aerosol-sea water reactivity. There is a direct relationship between the extent to which a trace metal is soluble in seawater and the extent to which it is held in the exchangeable fraction of an aerosol (Fig. 2.1). For Al and Fe in both end-member aerosols, <~10% of their total concentrations is in the form of exchangeable associations and both are also relatively insoluble in seawater. However, since both metals are present in relatively high concentrations in aerosols (3-8% by weight), even a solubility of a few percent can release considerable quantities of Al and Fe to seawater in a dissolved form. Mn has between ~20% and ~50% of its total concentration in the exchangeable fraction of each end-member aerosol and is relatively soluble, with ~35%-~50% of the total amount from each phase dissolving. Cu, Zn and Pb have significantly higher solubilities from the anthropogenic-rich than from the crust-rich end-member, due to their different speciation signatures in the two aerosol types. This is important, because it means that the aerosol seawater solubilities of Cu, Zn and Pb are reduced when crust-rich Saharan inputs perturb the anthropogenic-rich background aerosol over the MED.
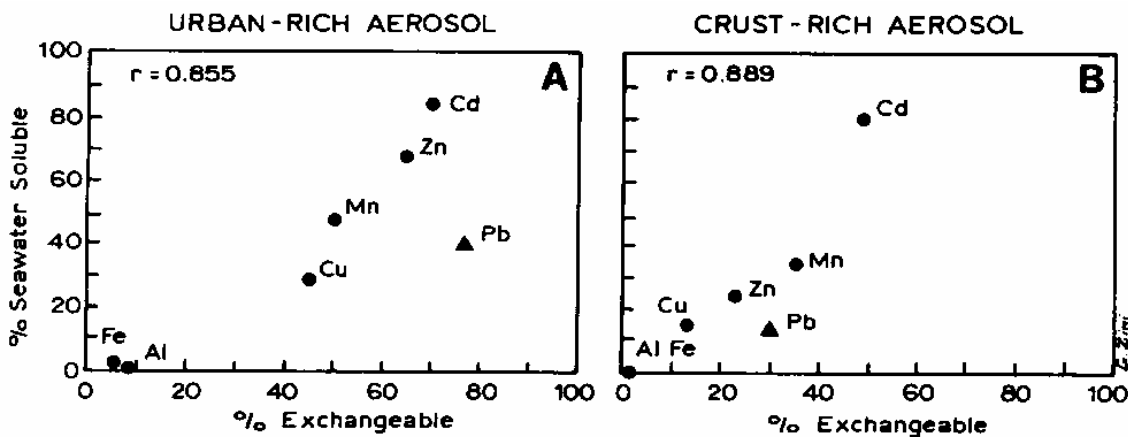

Fig. 2.1 - Relationship between percentages of total concentrations of trace metals soluble in seawater and in exchangeable associations in a) anthropogenic-dominated and b) crust-dominated aerosols. After CHESTER *et al.* (1993).

In the wet deposition mode, trace metal solubility is constrained initially by aerosol-rainwater reactivity since some metals are already in solution prior to the deposition of the aerosols on the sea surface.

Solubility is still a function of trace metal speciation in the parent aerosol, as illustrated by the dissolved/particulate speciation of a number of trace metals in rainwater from Western Mediterranean sites (Tab. 2.4). Al and Fe are generally insoluble in all types of rainwater (<20% of total concentrations), and Cd and Mn are relatively soluble (60-90% of total aerosol). Cu, Zn and Pb solubilities vary considerably from one rainwater sample to another and from site to site, e.g. that of Pb varies from ~20% at Sardinia to ~70% at Cap Ferrat.

Tab. 2.4 - Average dissolved/particulate speciation of trace metals in rainwaters from a number of Mediterranean Sea sites; data given as % of total trace metal concentration in dissolved phase.

	Cap Ferrat*	Tour du Valat*	Sardinia#	Corsica*
Al	18	19	2	8
Fe	-	11	3	13
Mn	60	63	-	67
Ni	54	58	-	-
Co	61	50	-	-
Cu	82	71	-	49
Zn	-	68	-	76
Pb	65	52	21	48
Cd	92	75	75	-

* GUIEU *et al.* (1997); # GUERZONI *et al.* (1997)

The speciation and solubility of trace metals is strongly affected by rainwater pH. Scavenging of anthropogenic-rich aerosols results in rainwater having pH values of <~4-5. In contrast, the scavenging of Saharan dust, with relatively high carbonate content, yields rainwaters with pH values of >~5. Many adsorption/desorption reactions are pH-dependent, particularly those affecting exchangeable trace metals. This may be illustrated for Pb in a series of rainwaters collected at Cap Ferrat (CHESTER *et al.,* 1990). The most striking feature in the pH vs solubility plot for Pb is the presence of the classical pH adsorption edge (Fig. 2.2), which is typical of adsorption/desorption processes at particulate-water interfaces and has been studied by various authors, in both rain and aerosols (CHESTER *et al.,* 1993; LIM *et al.,* 1994; SPOKES and JICKELLS, 1996). For Pb, this adsorption edge lies in the pH region ~4.8-~5.8. On the more acidic side, ~80% of total Pb is in the soluble form, whereas on the alkaline side only ~10% is soluble. However, some authors note that the low solubility region is defined by a relatively small number of points, reflecting the few cases studied of rain with pH >6 (LIM *et al.,* 1994; SPOKES and JICKELLS*,* 1996). This observation is important, given that these waters normally contain variable amounts of particulate material and that particle concentrations, grain-size, and physical surface characteristics (scavenged clays or silicate mineral aerosol) may also be important parameters in adsorption models of trace metals in rain (LIM *et al.,* 1994). In fact, aerosol dissolution experiments performed at particle concentrations ranging from 3 to 300 mg l^{-1} (the usual particle concentrations found in MED rainwater, see Tab.1.1) showed that Cd and Pb have low solubility at high particle concentrations (Fig. 2.3). The solubility of Pb was also found

to increase with increasing EF_{crust} values and with increasing content of the finest (<1µm) grain-size of the aerosols (GUERZONI *et al.,* in press).
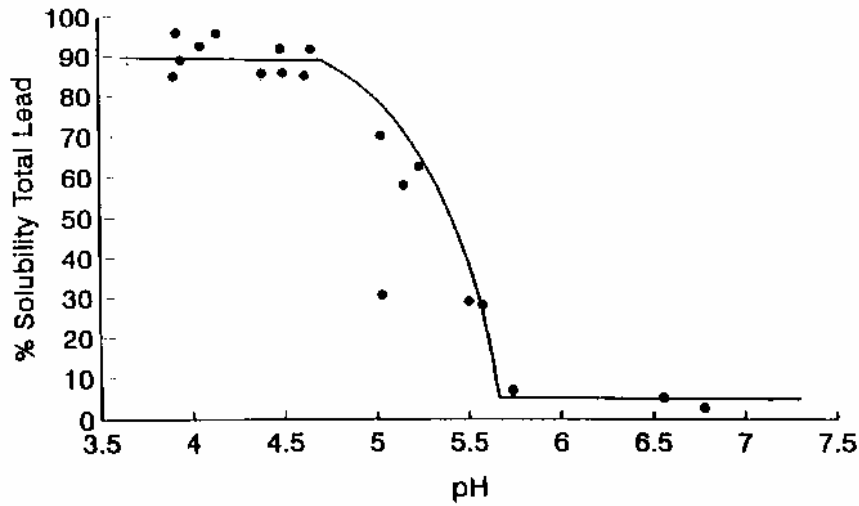

Fig. 2.2. - pH solubility of Pb in Western Mediterranean rainwaters (after CHESTER *et al.*, 1990).
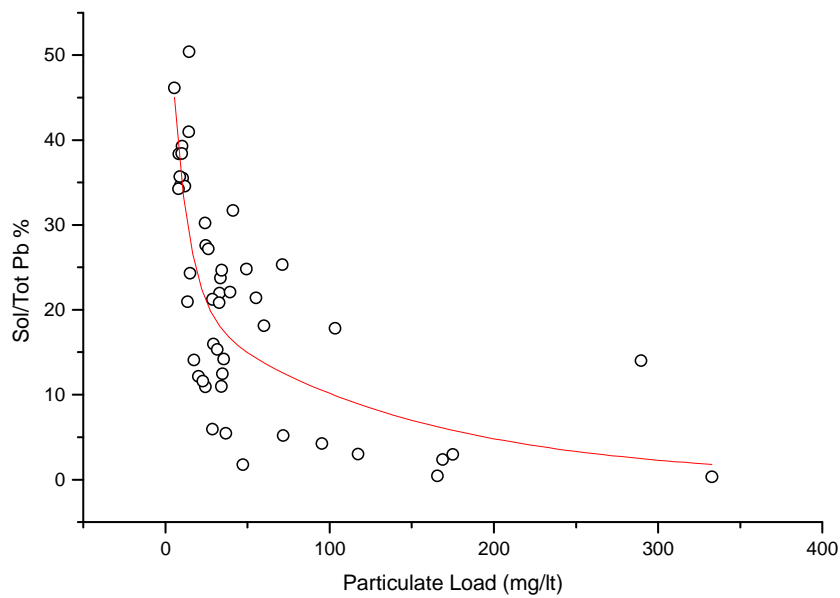

Fig. 2.3 - Lead solubility versus particulate load in aerosol dissolution laboratory experiment (from GUERZONI *et al.*, in press).

2.4. Atmospheric versus riverine inputs

Having identified atmospheric input as being important to the ocean, what problems remain in understanding the magnitude and significance of this input mode, with respect to riverine input? Aerosol undersampling problems may be remedied by increased sampling effort. Alternatively, atmospheric fluxes may be calculated from atmospheric transport and deposition models (ERDMAN *et al.,* 1994), using information on emission source strength (NRIAGU and PACYNA, 1988; GESAMP, 1989; AXENFELD *et al.,* 1992).

We present here two examples of comparison between riverine and atmospheric inputs using measurements made in the WMED and the Adriatic, Central Mediterranean (CMED).

2.4.1. Measurements.

The total atmospheric inputs of several trace elements and potential pollutants are compared with total riverine trace metal inputs for the Adriatic and the NW Mediterranean in Tab. 2.5.

Tab. 2.5 - Comparison between total inputs of atmospheric and riverine origin for Adriatic and NW Mediterranean (all data in ton yr^{-1}). * Al and Fe: ton x 1000; # Adriatic Sea area: 112,000 km^2; from ROSSINI and GUERZONI (1996); § NW Mediterranean Sea area: 180,000 Km^2, from GUIEU *et al.* (1997).

tons year^{-1}		Al*	Fe*	Cd	Pb	Cu	Ni	Zn
Adriatic[#]	atmosphere	29	14	18	311	489	148	177
	Po river	86	74	7	151	281	514	935
NW Med.[§]	atmosphere	97	151	126	579	486	162	12,600
	Rhône & Ebro rivers	441	232	13	318	505	450	1545

The data indicate that the atmosphere supplies 16-90% of the total input of these elements. When dissolved fluxes are compared (the form most likely to impinge on surface water biogeochemical cycles), the influence of atmospheric input is even more pronounced (Tab. 2.6).

Tab. 2.6 - Comparison between dissolved inputs of atmospheric and riverine origin for Adriatic (area: 112,000 km^2) and NW Mediterranean (area: 180,000 Km^2). # Adriatic Sea: from ROSSINI and GUERZONI (1996); § NW Mediterranean Sea: from GUIEU *et al.* (1997).

tons year^{-1}		Al	Fe	Cd	Pb	Cu	Ni	Zn	PAH	PCB
Adriatic[#]	atmosphere	1039	573	13	152	332	116	1560		
	Po river	60	30	4	10	66	148	215		
NW Med.[§]	atmosphere	10	16	99	252	189	81	6813	45	12
	Rhône & Ebro rivers	1	1	2	8	175	115	105	15	1

For example the atmosphere is 5-50 times more important than rivers for dissolved Zn fluxes and 15 - 30 times more important for Pb fluxes. A similar pattern is seen for Cu. The dramatic difference between total particulate and dissolved fluxes underscores the important role played by speciation of trace elements in rainwater in determining their flux to the surface ocean.

2.4.2. Models.

Only by using models can we extend the same comparison to each of the three basins of the MED (Tab. 2.7). This comparison is meant to show the same approach as the two tables above but is extended to other basins for total fluxes.

Table 2.7 - Comparison of total riverine (R) and atmospheric (A) inputs to Mediterranean Sea (all in tons yr^{-1}). Data on Pb and Zn riverine inputs from UNEP (1984), on atmospheric input from ERDMAN *et al.* (1994) and GESAMP (1989).

Sub-basin	Area (10^{6}km^2)	Pb R	Pb A	Zn R	Zn A
Western Med	0.84	2200	3072	9200	1125
Central Med	0.80	1770	2757	10700	809
Eastern Med	0.70	850	1605	4800	590
Total	**2.34**	**4820**	**7404**	**24700**	**2524**
% atmosphere			*61*		*9*

Available estimates of riverine and atmospheric inputs were computed on the basis of average pollutant concentrations and mean water discharges for rivers (UNEP, 1984) and by applying a Eulerian-Lagrangian model for atmospheric transport and deposition (ERDMAN *et al.,* 1994).

Several sources of errors are associated with these estimates. An example is given in Tab. 2.8, showing a comparison between measured and model data for Pb and Zn in the Adriatic (equivalent to WMO area MT5; see ERDMAN *et al.,* 1994) and north-western Mediterranean (equivalent to WMO area MT2; see ERDMAN *et al.,* 1994). In these models, the authors state that the discrepancy between regional mean values for Pb does not exceed 20%, but very often individual data are less reliable. For Zn, the total underestimation of mean values by the models may be 10 times lower, mainly because of underestimation of the emission strength .

These comparisons of modelling results with measurement data for atmospheric deposition should only be considered as approximate, for the following reasons (EMEP, 1994): i) models give grid square (e.g. 150x150 km) average values and measurements give point values, and variations between measurement and model data increase with increasing grid size and decreasing averaging time; ii) as completeness of measurement data should be 75-80% over a rather long period of time (e.g., at least one month) to be used for comparison with modelling results, better spatial and temporal data rage is needed; iii) measurement sites should be representative for the whole grid square

(meteorological conditions, surface characteristics, local pollution sources, etc.); iv) several monitoring sites are needed for a square of 150x150 km and correlation analysis between sites should be applied, taking into account seasonality, mixing, time scale, meteorology, emission and topography; v) measurement and modelling data used for comparison purposes are sometimes made at different times (or even in different years) and the year-to-year variability of meteorological conditions introduces uncertainty into single-year model (or measurement) estimates; vi) emissions used for modelling are rather uncertain and sometimes underestimated, and are mainly based only on annual estimates from major sources without the required temporal and spatial distributions.

Tab. 2.8 - Comparison between atmospheric (measured and modelled) and riverine inputs (measured and estimated).

Region	Input		Pb tons y^{-1}	Zn tons y^{-1}	Reference
Adriatic	atmospheric	measured	311	177	ROSSINI and GUERZONI (1996)
		model	871	246	ERDMAN *et al.* (1994)
	riverine	Po river measured	151	935	ROSSINI and GUERZONI (1996)
		estimated	1300	7900	UNEP (1984)
NW Med	atmospheric	measured	579	12600	GUIEU *et al.* (1997)
		model	999	337	ERDMAN *et al.* (1994)
	riverine	Rhône & Ebro measured	318	1545	GUIEU *et al.* (1997)
		estimated	800	2400	UNEP (1984)

It may be seen that atmospheric data are in agreement within a factor of 2-3, whereas huge differences are evident for riverine inputs. Some of these differences are due to the reduction in run-off and discharge over the last 10-20 years, not always accounted for in the models. Furthermore, riverine model data are derived from run-off estimates and contain few real measurements, therefore providing only an order-of-magnitude estimate of the elemental input for the MED basin. In addition, the differences between models and measured data may be due to the behaviour of elements in estuarine areas. The chemical behaviour of elements in this zone is very difficult to generalise. For some elements there is removal from the water column in the estuarine zone while for others there is no effect. In some cases (e.g. Cd), there is addition of the element to the dissolved phase as a result of the competitive desorption of Cd bound to the surface of suspended particulate material by seawater ions. While the behaviour of a particular element can be characterised in a particular estuary, different physico-chemical regimes (e.g. pH, ionic strength, presence of dissolved organic matter, etc.) in a different estuary can lead to different behaviour in the mixing zone.

2.5. Case studies.

2.5.1. The atmospheric "signature" in seawater. For some reactive trace elements including Al, Mn and most notably Pb (BRULAND *et al.*, 1991; BUAT-MENARD, 1993; PATTERSON and SETTLE, 1987),

the shapes of dissolved oceanic profiles with surface water concentration maxima suggest that atmospheric input is of major importance. For other elements which are not so rapidly removed from seawater by scavenging processes, internal biogeochemical cycles mask such input signals.

Al and Fe. It has been shown above that Al and Fe have only relatively low solubilities from aerosols but, since they are present in large concentrations, even low solubility can deliver significant quantities to the dissolved seawater pool from dust pulses.

The effect of dust deposition of Al on MED surface waters is dramatically visible in its effect on the surface water concentrations. The extremely high concentration of this element in crustal materials (8.1%; TAYLOR, 1964), and its low concentration in seawater makes it a particularly good tracer of the partial dissolution of eolian dust in MED surface waters. In fact, as a result of biological and convective transport, the deep waters of the MED have the highest concentrations of dissolved Al of any basin in the world, consistent with their receiving the greatest rate of deposition of eolian material. The effect that this has on the Al budget has been recognised by several workers (HYDES *et al.,* 1988; MEASURES and EDMOND, 1988; CHOU and WOLLAST, 1997), the latter indicating that the partial deposition of eolian dust in the WMED was responsible for some 20 times as much input of Al as that supplied by rivers. That the eolian input is basin-wide is shown by the progressive build-up of Al from west to east along the advective flow path of the incoming Atlantic surface water (Fig. 2.4).
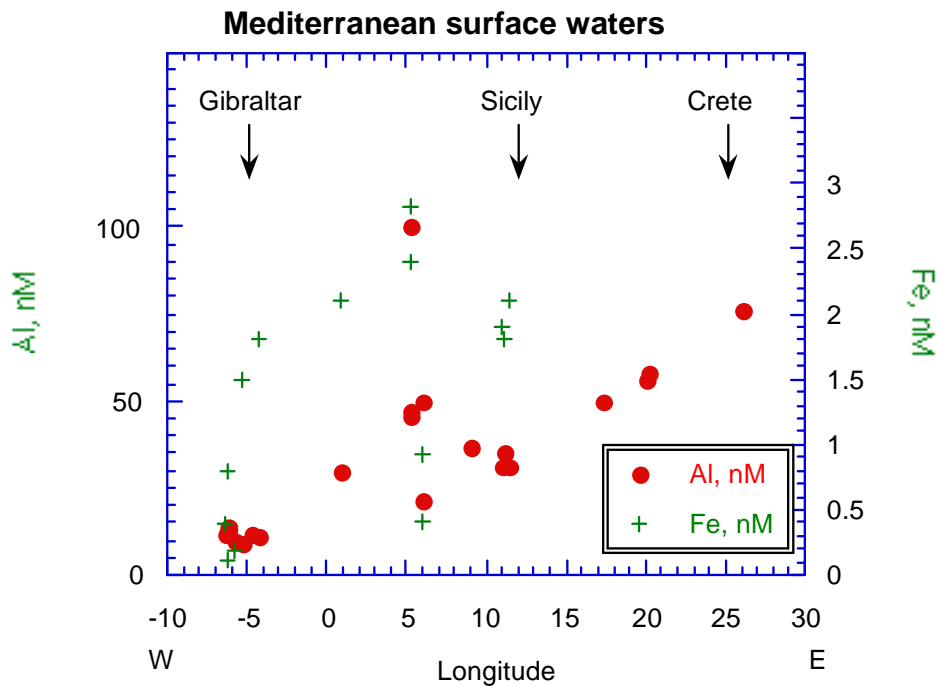

Fig. 2.4 - Distributions of dissolved Al and Fe in surface waters of Mediterranean.

In this figure, all post-1980 surface water Al values in the open Mediterranean are plotted as a function of longitude. Data from the region of the Gulf of Lions are excluded, to eliminate the local influence of the Rhone discharge. In addition, early Corsican nearshore data are excluded, to eliminate local artifacts.

The data distribution is quite distinctive in that there is an unmistakable increase in Al concentrations from 9-13 nM at the Strait of Gibraltar (6 W) to ~75 nM at 26 E in the eastern basin. The anomalously high value at ~5 E (100 nM) results from elevated deep water mixing into the surface waters in December 1988, during a convection episode in the Western Mediterranean Deep Water formation region. The general trend indicates something of the order of a 60-nM Al enrichment of inflowing Atlantic surface waters during their eastward transit from the Strait of Gibraltar to the eastern basin.

The magnitude of this Al enrichment may be compared with estimates of atmospheric deposition to the region. GUIEU *et al. (*1997), using atmospheric data from coastal collection sites, estimated an annual deposition of some 0.38 to 3.8 mmoles of dissolved Al m^{-2} to the surface waters of the north-west Mediterranean. Such an input into a 50-m mixed layer, over the advective flow path of the Atlantic water, could easily raise Al concentrations in inflowing surface water to the values seen in the eastern basin over the time-scales of surface water renewal in the Mediterranean (1-10 years).

While the impact of dust is readily observed and is quantified in the Al signal, its effect on Fe concentrations is more difficult to quantify. The largest problem is the small data base of reliable measurements for Fe in the Mediterranean. Fig. 2.4 plots all the surface water dissolved Fe data of MORLEY *et al. (*1997) available in the EROS-2000 data base which appear to be oceanographically consistent. The data of MORLEY *et al. (*1997) show a wide range of concentrations from 0.11 nM in the Strait of Gibraltar to 2.83 nM south of the Gulf of Lions. However, unlike the Al, there is no clear geographic trend associated with these values. Nevertheless, it may be stated that, on the basis of this data set, Fe levels are generally above 1 nM within the Mediterranean. It therefore seems reasonable to conclude that Fe cannot be considered as limiting factor to phytoplankton. This appears to be probable merely on the basis of available nutrients. Since the surface Mediterranean is low in nutrients, Fe demand is similarly low. Using Fe limiting conditions and assuming a C:N ratio of 6.7, 0.5 nM of Fe (at the low end of the observed amount of Fe in 1-L of seawater) is capable of removing 7.5 µM of N from surface waters, an extremely large amount of N to be found in 1-L of seawater in this nutrient-impoverished sea.

In summary, dust input to the Mediterranean clearly affects surface water trace element budgets, and this is most visible for Al for which a large data base of modern observations exists. Although surface water Fe concentrations in the Mediterranean also appear elevated, the small size and geographical extent of the existing data base precludes direct association of these values with dust deposition events. It is unlikely that dust deposition to the surface Mediterranean would spur primary production through either the relief of Fe-limiting conditions or the provision of a bioactively reduced Fe species.

2.5.2. Pb in atmosphere and seawater. The EROS 2000 data base on lead concentrations over the period 1989-1993 gave an average of 100pM in surface waters and 80 pM in bottom waters. A mass balance for the WMED has been computed (MILLIMAN and MARTIN, 1997), and the output/input ratio for lead in the whole basin is 0.8, with a residence time of 5.2 years (water residence time being ~15 years). A tentative budget of dissolved lead in the WMED (WOLLAST, pers. comm.) indicates an accumulation in the water of 440 tons yr^{-1} for the period 1970-1985, related to the constant increment in consumption of leaded gasoline in that period.

In contrast, a recent paper (MIGON and NICOLAS, 1998) shows a reduction (over the period 1987-1995) of atmospheric fluxes of dissolved Pb from 3.5 to 1.5 mg m^{-2} yr^{-1}, and of surface water concentrations in the WMED (central Ligurian Sea) from 300 to 120 pM. The amount of Pb in inflowing rivers has probably decreased in a similar way to the atmospheric input. However: i) the natural Pb component is probably higher in rivers than in the atmosphere, because of soil erosion; ii) a previous study (MIGON, 1993) showed that riverine Pb fluxes are far lower than atmospheric ones, and the loss of atmospheric Pb was estimated at >90%; iii) Pb dissolved in fresh water tends to precipitate and settle close to the river mouth (SHARP and NARDI, 1987; WINDOM *et al.,* 1988; DORTEN *et al.,* 1991), which lowers the role of the riverine contribution to offshore marine Pb concentrations. These results confirm the importance of the atmosphere in delivering Pb to surface waters and in controlling its concentration. Figure 2.5 illustrates the temporal evolution of dissolved Pb concentrations in surface waters (upper 100 m), together with mean atmospheric fluxes. The two curves have the same shape, which *a posteriori* indicates that the introduction of automotive Pb into the marine environment essentially occurs through the atmospheric pathway.
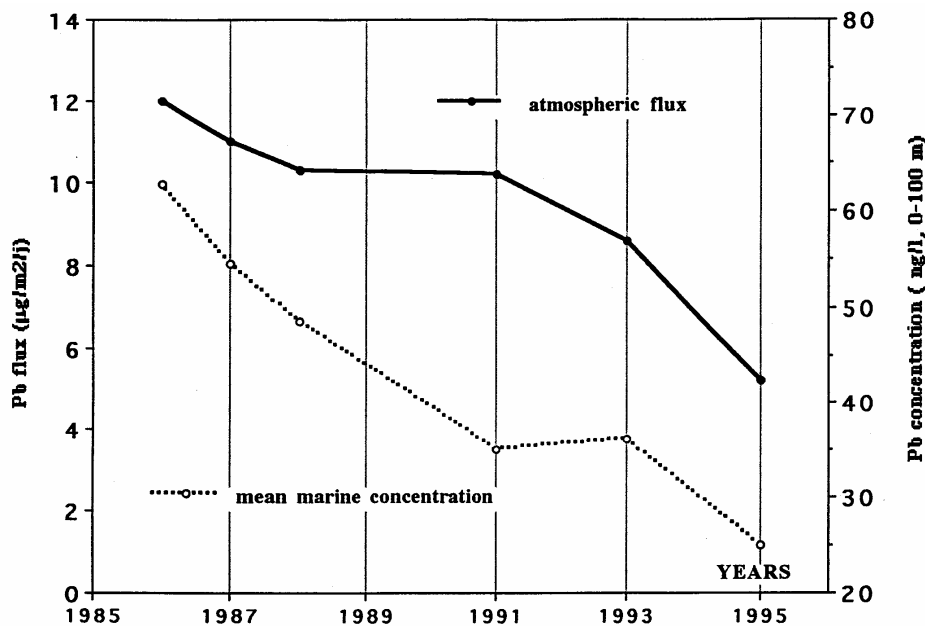

Fig. 2.5 - Pb atmospheric flux and mean marine Pb concentrations (0-100 m) (from MIGON and NICOLAS, 1998).

3. Atmospheric input of nutrients: estimates and impacts

The importance of the atmosphere as a source of nutrients, especially nitrogen, for terrestrial ecosystems was recognised as a by-product of studies of the impact of acid rain in the early 1980s. At the end of that decade, atmospheric nitrogen deposition to marine systems began to be investigated and its importance for the global ocean was assessed (DUCE, 1986). For example, it has been noted that the atmospheric input of nitrogen may be partly responsible for the eutrophication of estuarine or coastal waters and the appearance of harmful algal blooms, by either direct input or through the watershed (FISHER *et al.,* 1988; MALLIN *et al.,* 1993; PAERL *et al.,*1993).

Despite early observations of P limitation (FIALA *et al.,* 1976; BERLAND *et al.,* 1973, 1980), recent works suggest that MED surface waters are nitrogen-limited (ANDERSEN and NIVAL, 1988; OWENS *et al.,* 1989). In fact, there is growing evidence that the EMED is phosphorus-limited (KROM *et al.,*1991) and that the WMED is probably N-limited (RAIMBAULT and COSTE, 1990; THINGSTAD and RASSOULZADEGAN, 1995), or that limitation shifts from nitrogen to phosphorus and *vice versa* depending on the period of the year (FIALA *et al.,* 1976, DOLAN *et al.,* 1995) or the area considered (WOODWARD and OWENS, 1989). The unique high levels of N/P ratios in the MED (20/27) compared with other open ocean averages (15) may reflect this situation, and are probably evidence of P limitation.

3.1. Atmospheric inputs of nitrogen to the Mediterranean

While there are many natural sources of fixed nitrogen to the atmosphere - NO_3 from soils and NH_3 from wetlands - in the northern hemisphere the main sources are anthropogenic (NO_x from industrial combustion and vehicle traffic, HNO_3 from vehicle traffic, NH_3 emissions from intensive farming). The most abundant data are for inorganic wet deposition. Data for the WMED and EMED are listed in Table 3.1.

Tab. 3.1 - Dissolved inorganic nitrogen (DIN) wet deposition (a: LOŸE-PILOT *et al.*, 1990a; b: MIGON *et al.*, 1989; c: LOŸE-PILOT *et al.*, 1990b; d: GUERZONI *et al.*, 1993; e: LE BOLLOCH and GUERZONI, 1995; f: HERUT and KROM, 1996).

Studied site	Field data		Best estimates in sub-basins			Mediterranean	
	Period	Range (annual basis) $\mu mol\ m^{-2}\ d^{-1}$	NWMED	WMED	EMED		
			$\mu mol\ m^{-2}\ d^{-1}$			$\mu mol\ m^{-2}\ d^{-1}$	$10^{10}\ mol\ yr^{-1}$
French coast - Camargue[a]	feb 88/jul 89	73					
French coast - Cap Ferrat[b]	86/87	119/142					2,5 / 7,5
Corsica - Bavella[c]	84/86	126 / 150	100	80	50	50 / 80	4,6 / 7,3
Sardinia - C.Carbonara[d]	91/94	47					
Sardinia - Torregrande[e]	92/93	41 / 56					
Israel - Haifa+ South-EMED[f]	92/95	65			59	72	6,1

Atmospheric input of wet inorganic nitrogen. The average wet dissolved inorganic nitrogen (DIN) flux to the north-west Mediterranean of ~100 µmol N m^{-2} d^{-1} (LOŸE-PILOT *et al.,* 1990a) is somewhat higher than that to the south-east Mediterranean, which is ~60 µmol N m^{-2} d^{-1} (HERUT and KROM, 1996), the value for the whole Mediterranean being between 50 and 80 µmol N m^{-2} d^{-1} (LOŸE-PILOT *et al.,* 1990a). Nitrate and ammonium contribute almost equally to the DIN, while nitrite is normally less than 3%.

Atmospheric input of dry inorganic nitrogen. Dry deposition of inorganic nitrogen includes gas and particulate deposition. Only annual average data are available for atmospheric particulate inorganic nitrogen species. Values in the NWMED are 1.71 and 0.85 µg m^{-3} for NO_3^- and NH_4^+, respectively (KLEIN, 1998), and in the EMED 1.51 and 0.97 µg m^{-3} for NO_3^- and NH_4^+ (MIHALOPOULOS *et al.,* 1997). These coastal values are in good agreement with the mean concentrations of 1.45 and 1.22 µg m^{-3} for NO_3^- and NH_4^+ obtained by MEDINETS (1996) from shipboard sampling over the whole Mediterranean. The reported values for particulate dry deposition depend on the deposition velocities chosen for NO_3^- and NH_4^+, the best estimate for the NWMED being 25 µmol N m^{-2} d^{-1} (KLEIN, 1998).
Gas concentration measurements are very scarce, especially for NH_3 which is assumed to be negligible regarding N deposition to the Mediterranean. The few HNO_{3gas} measurements are from urban sites.
Fig. 2.6 shows the partitions of various inorganic species and forms in the atmospheric deposition of nitrogen for the NWMED.
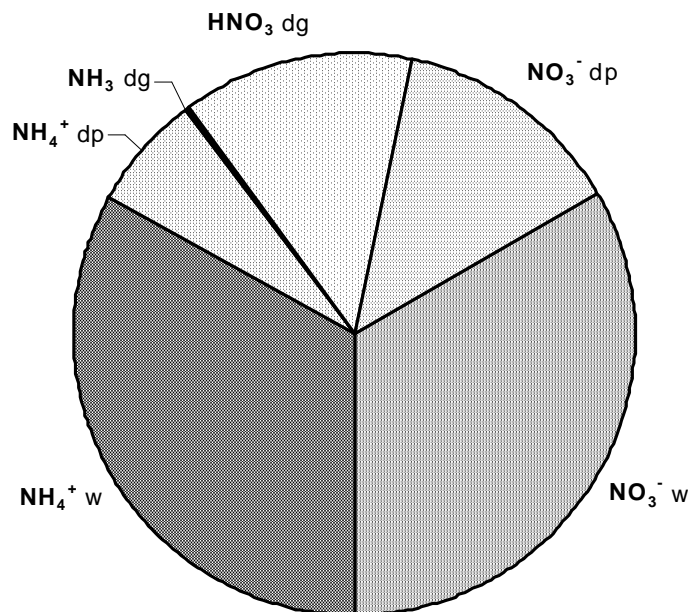

Fig. 2.6 - Relative importance of atmospheric inputs of different N species to NW Mediterranean; w=wet dp=dry particulate, dg=dry gaseous.

Total inorganic nitrogen deposition (Table 3.2). If only particulate dry species are taken into account, nitrogen dry deposition represents 25-33% of wet deposition in the north-west basin (LOŸE-PILOT *et al.,* 1990, KLEIN, 1998); taking HNO_{3gas} into consideration would increase the influence of dry deposition to equal wet deposition in coastal urbanised zones. Dry deposition equal to half that of wet deposition seems to be a realistic assessment for the open sea. Results are summarised in Table 3.2, which also lists data from the UNEP Mediterranean Pollution (MED POL) Project (computed from models) for 1991 (ERDMAN *et al.,* 1994*;* UNEP, 1984). Total inorganic nitrogen deposition varies between 214 µmol N m^{-2} d^{-1} for the Adriatic to about 48 µmol N m^{-2} d^{-1} for the Central Mediterranean (UNEP zone VII) (ERDMAN *et al.,* 1994), agreeing well with the previously estimated values of 105 µmol N m^{-2} d^{-1} for the WMED and 65 µmol N m^{-2} d^{-1} for the EMED (LOŸE-PILOT *et al.,* 1990b).

Distance from the source and climatological conditions appear to be the major factors which control nitrogen inputs. If the DIN flux to the southern oceans, ~ 6 µmol N m^{-2} d^{-1}, represents the natural background level, then 90% of the total DIN flux into the Mediterranean is of anthropogenic origin.

Tab. 3.2 -Total nitrogen deposition (a: LOŸE-PILOT *et al.*, 1993, b: KLEIN, 1998, c: LOŸE-PILOT, 1998, d: ERDMAN *et al.*, 1994); p = particulate, g = gaseous species.

	Best estimates				
	NWMED	**WMED**	**EMED**	**Mediterranean**	
	µmol m^{-2} d^{-1}	µmol m^{-2} d^{-1}	µmol m^{-2} d^{-1}	µmol m^{-2} d^{-1}	10^{10} mol yr^{-1}
Field data					
dry$_p$= 1/3 wet[a,b]	125	105	65	65 / 105	5,6 / 9,0
dry$_{p+g}$= 1/2 wet[c]	150	120	75	75 / 120	6,4 / 10,2
Model					
(UNEP MAP 94)[d]	117	107	80 without Adriatic: 69	89	7,6

Organic nitrogen. The importance of organic nitrogen in total atmospheric nitrogen deposition has recently been re-evaluated; it may represent half of the input of inorganic forms on a regional scale and be equal to them for global ocean (CORNELL *et al.,* 1995; DUCE *et al.,* 1997). The source of organic nitrogen is not known, but CORNELL *et al. (*1995) believe that a large fraction of it is anthropogenic.

The few measurements of organic nitrogen content in the Mediterranean atmosphere (SPITZY *et al.,* 1990; LOŸE-PILOT *et al.,* 1992) indicate that total amino acid concentrations in aerosols and rainwater are small (<5%) relative to inorganic species. It is clear that further studies are needed to assess the content, speciation and bioavailability of organic nitrogen in general and in the Mediterranean atmosphere in particular.

3.1.1. Atmospheric versus riverine inputs of nitrogen in the Mediterranean. The DIN atmospheric input to the NWMED is in the same range as the Rhone input, which is the major water and nutrient riverine output to the WMED. If the entire WMED is considered (LOŸE-PILOT *et al.,* 1990b), then atmospheric

input - derived from field data - is probably higher than that of rivers. Atmospheric input of N (1084×10^3 tons yr^{-1}) is equal to the riverine input (1000×10^3 tons yr^{-1}) for the whole Mediterranean according to UNEP/WMO estimations (BASHKIN *et al.,* 1997), the atmospheric input being predominant in the southern zones. If the fraction of riverine input which is derived from the atmosphere is taken into account, the atmospheric input is ~60% of the total continental supply of nitrogen to the Mediterranean (BASHKIN *et al.,* 1997).

Due to the fact that riverine nutrients are removed by biological activity in estuarine and proximal coastal zones, atmospheric input is probably the main source of nitrogen for the open sea, even in the northern zones of the Mediterranean.

3.1.2. Impact of atmospheric input of nitrogen on primary production. Atmospheric input of N contributes to new production (DUGDALE and GOERING, 1967; EPPLEY and PETTERSON, 1979; DUCE, 1986), which is the primary production fuelled by nutrients originating outside the photic zone, as opposed to production fuelled by recycled nutrients from within the photic zone. Assuming that the assimilation of nitrogen is in the Redfield ratio to carbon (16/106), then the atmospheric input of nitrogen may account for new production of about 3.8 g C m^{-2} y^{-1} in the NWMED, 2.5 g C m^{-2} y^{-1} in the SWMED, and 2.1 g C m^{-2} y^{-1} in the SEMED.

For coastal zones such as the Gulf of Lions, where total primary production is as high as 130-180 g C m^{-2} y^{-1} (MOREL *et al.,* 1990; TUSSEAU and MOUCHEL, 1995) and new production is approximately one-third of the total, then the atmospheric input of nitrogen represents only about 6-10% of new production, while the Rhône river provides ~50%. However, in oligotrophic zones in the WMED, primary production is about 50 g C m^{-2} y^{-1} and new production is as low as 5 g C m^{-2}.yr^{-1}. In this case, the atmospheric N input of 2.5-3 g C m^{-2} y^{-1} represents up to 60% of new production. This contribution is somewhat lower in the oligotrophic zones of the EMED, where new production has recently been re-estimated at 16.7 g C m^{-2} y^{-1} (KROM *et al.,* 1991). In this case, the atmospheric input of nitrogen, 2.1 g C m^{-2} y^{-1}, represents ~12% new production.

3.2. Atmospheric input of phosphorus

The atmospheric input of phosphorus has received less attention than that of N, as it is assumed to be less important. The atmospheric input of dissolved inorganic phosphorus to Cap Ferrat is estimated at 1.4 µmol m^{-2} d^{-1} and to be between 0.4 and 1.4 µmol m^{-2} d^{-1} for the NWMED (MIGON *et al.,* 1989). Total inorganic phosphorus deposition to the WMED was determined to be 3.5 µmol m^{-2} d^{-1} from 3 years of samples collected in Corsica. Crustal material made up 40% of this flux, and the dissolved fraction was estimated to be between one- and two-thirds of the total (BERGAMETTI *et al.,* 1992).

The wet deposition of total inorganic phosphorus to the SEMED, estimated from 2 years of measurements on the northern coast of Israel was 0.6 µmol m^{-2} d^{-1} and dry deposition was 1.2 µmol m^{-2} d^{-1} (HERUT and KROM, 1996), giving a total rate of 1.8 µmol m^{-2} d^{-1}.

3.2.1. Saharan dust and phosphorus.

Phosphorus values of Saharan dust range from 0.04% found in the SEMED to 0.07% from Libyan desert material (HERUT and KROM, 1996). Values as high as 0.25-0.40 % were found in Saharan dust collected in the NWMED (LOŸE-PILOT, unpublished results). A mean content of 0.25 % gives a mean phosphorus deposition from Saharan dust in this region of 2.8 μmol m^{-2} d^{-1}. However, the question of the solubility and bioavailability of this phosphorus is still open. According to KROM *et al.,* (1991), Saharan dust may act as a trap for soluble phosphorus by adsorption of PO_4^{3-} on to Fe-rich particles, whereas LEPPLE, (1971) found that up to 8% of Saharan dust phosphorus is soluble in seawater. From a partitioning study between crustal and anthropogenic phosphorus, BERGAMETTI *et al.,* (1992) estimated that between 1.2 and 2.7 μmol P m^{-2} d^{-1} is dissolved in seawater from atmospheric input and is available for biota. Similar values (1.2 μmol P m^{-2} d^{-1}) were obtained from calculations for the EMED, assuming a dust flux of 36 g m^{-2} yr^{-1}, with 0.4% P and a solubility in seawater of 10% (see section 4.1). Table 3.3 shows estimates of the dissolved inorganic phosphorus (DIP) inputs to the WMED (1.5 μM P m^{-2} yr^{-1}) and EMED (0.6 μM P m^{-2} yr^{-1}), and Table 3.4 compares total inorganic phosphorous (TIN) atmospheric inputs with riverine P discharge estimates.

Tab. 3.3 - Dissolved inorganic phosphorus (DIP) and total inorganic phosphorus (TIP) deposition (values in μmol m^{-2} d^{-1}).

	DIP	TIP
Cap Ferrat [a]	1.4	--
NWMED [b]	0.4-1.4	--
Corsica [c]	1.2-2.7	3.5 (2.1 anthro+1.4 Sahara)
Corsica [d]	---	2.8 Sahara
avg. WMED	*1.5*	*3 (0.035 gP m^{-2} yr^{-1})*
EMED [e]	0.6	1.8 (0.021 gP m^{-2} yr^{-1})

a, b: MIGON (1989); c: BERGAMETTI *et al.* (1992); d: LOŸE-PILOT, unpublished results; e: HERUT and KROM (1996)

Table 3.4 - Comparison of riverine (R) and atmospheric (A) inputs of nitrogen and phosphorus (all in tons *10^3 yr^{-1}). Data on N and P riverine inputs from VOLLENWEIDER *et al.* (1996); on N atmospheric input from ERDMAN *et al.* (1994); on P atmospheric input: from average TIP fluxes in three sub-basins (west to east) of 0.035-0.028-0.021 g P m^{-2} yr^{-1}, respectively.

Sub-basin	Area (10^{6}km^2)	Nitrogen R	A	Phosphorus R	A
WMED	0.84	577	459	78	29
CMED	0.80	212	346	29	22
EMED	0.70	223	263	30	15
Total	**2.34**	**1011**	**1068**	**137**	**66**
% atmosphere			*51*		*33*

3.2.2. Impact of atmospheric phosphorus on primary production.

Taking the two values from BERGAMETTI *et al.,* (1992) and applying the Redfield ratio (C/P =106/1) gives potential carbon production due to atmospheric dissolved phosphorus input of 0.56 to 1.25 g C m^{-2} yr^{-1}, that is, 11-25% of the new production of the very oligotrophic zones of the WMED, and one to a few percent for the other more productive zones. The impact of the atmosphere therefore seems to be low for phosphorus; certainly lower than for nitrogen.

The high N/P ratio of atmospheric input (~ 70) may be responsible for the high N/P ratio (20-27) observed in Mediterranean seawater (HERUT and KROM, 1996).

3.3. Conclusions and hypotheses

The relative importance of atmospheric input of nutrients to the Mediterranean increases from the shoreline to the open sea with the decreasing influence of riverine inputs, and from active mixing zones (margin "upwellings", frontal zones) to oligotrophic "stable" zones. On an annual scale, the nitrogen atmospheric input is significant for oligotrophic zones, in which it may account for up to 60% of new production, whereas atmospheric phosphorus may account for a maximum of 25%.

It is evident that the impact of the atmospheric input of nutrients to the open Mediterranean is difficult to detect, and would in any case be negligible during the period of intense primary production due to mixing with deep rich waters. But during the summer and early fall stratification of the Mediterranean, atmospheric inputs represent a non-negligible source of nutrients (up to 4000 µmol N m^{-2} d^{-1}), which may trigger small but detectable phytoplankton blooms (Fig. 3.1), as reported by MARTIN *et al. (*1989).
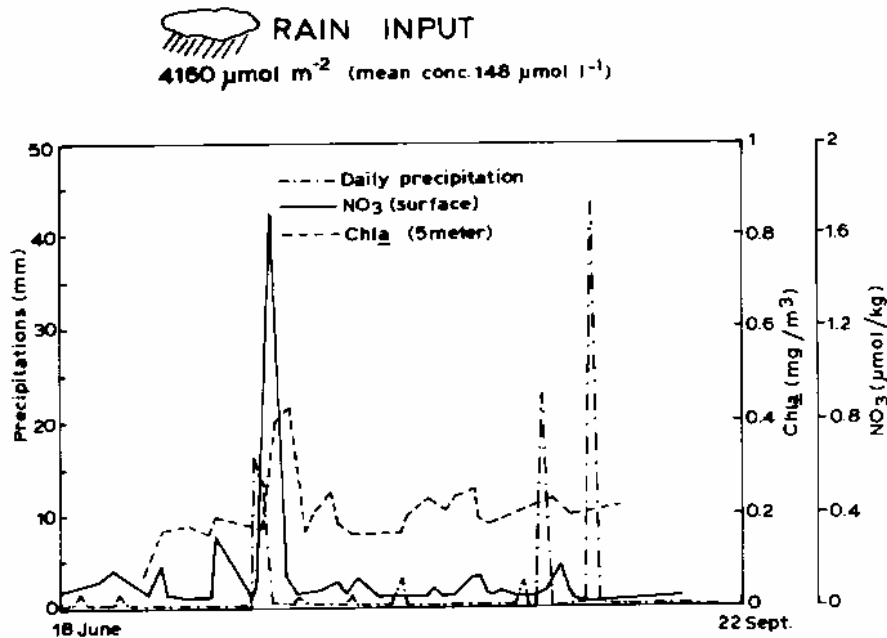

Fig. 3.1 - Wet atmospheric input of nitrogen and its effect on productivity (from MARTIN *et al.*, 1989).

In this respect, annual atmospheric N budgets may have little significance, but the episodic character of the atmospheric supply may be significant over short time-spans. An example of this is the wet atmospheric N deposition pulse which was studied at Villefranche (MIGON *et al.,* 1989). In this case, prior to deposition, oligotrophic conditions persisted and the upper 18 m of the water column was stratified by a low salinity layer. After the deposition event, the atmospheric N signature was clearly observed for 21 days. Neglecting the role of phosphorus, this input of 0.23 µmol N l^{-1} would theoretically be able to induce new production of 16 mg C m^{-2} day^{-1}.

In the same way, the sporadic input of Saharan dust may be a source of phosphorus, especially when originating from mixed (anthropogenic/Saharan) rains, in which case phosphorus would be partly desorbed and dissolved from the dust. It has been suggested that some summer algal blooms may be explained by such Saharan dust fallout (see section 4.1) (DULAC *et al.,* 1996).

The role of Saharan dust still needs careful assessment, as it may be an important source of phosphorus and iron (see below). The processes and magnitude of phosphorus and iron dissolution from desert dust and their biological impact are important topics to be investigated in the oligotrophic Mediterranean. Two examples of this will be described in the next section.

4. Potential effects of atmospheric input on surface ocean biogeochemistry: preliminary speculations

It appears that atmospheric inputs of metals and nutrients to the MED are of similar magnitude to fluvial inputs, although there are several uncertainties which currently prevent us from quantifying the magnitude and chemical effects of these inputs. The next question that should be addressed is whether they are of significance to biogeochemical cycles in the ocean. We will discuss below two examples in which it seems that atmospheric inputs coincide with a biological response.

4.1 Meteosat and CZCS: a case of P-fertilisation?

DULAC *et al. (*1996) presented a study combining monitoring of desert aerosol from Meteosat and of marine phytoplankton from CZCS (Coastal Zone Colour Scanner) in the WMED during summer 1983. Daily Meteosat images in the solar spectrum (visible channel) were used to quantify African dust transport, following the method described in MOULIN *et al. (*1997a). The CZCS multichannel was used to monitor marine biology activity in the WMED. Estimates of phytoplankton abundances were based on the algorithm of MOREL (1988) using ratios of seawater reflectances at 0.44 and 0.55 µm after correction for atmospheric effects (ANDRÉ and MOREL, 1991).

DULAC *et al. (*1996) observed a particularly strong desert dust transport event at the end of July 1983 (peak on Julian day 209), which yielded a strong dust flux to Mediterranean waters, with a cumulative input up to 1.5 g m^{-2} during the week, as shown in Fig. 4.1. They also analysed about one hundred CZCS images of the Ligurian Sea during the same period, and averaged chlorophyll estimates in a

region of 100x100 km^2 near the DYFAMED station (corresponding to about 10000 CZCS pixels). Any images in which more than half the CZCS pixels were cloudy or in which the geometric standard deviation of the pixels was larger than 1.5 were rejected. Any images in which the satellite signal was contaminated by high desert dust loads were also eliminated, using the near-infrared channel (0.75 μm) of the CZCS. In all, nearly 90% of the initial images were rejected; the resulting maps of phytoplankton concentrations are shown in Fig. 4.2. The peak of dust input (equivalent to approximately 9 μmol P m^{-2}) was followed, two weeks later, by a significant increase in phytoplankton concentrations, with a peak value of about 0.5 mg m^{-3} observed on August 16 (day 228). A response time of one week seems reasonable for phytoplankton growth in natural conditions. It is unlikely that the observed increase in phytoplankton concentration was connected with a decrease in summer surface water stratification, since during the whole period the surface wind speed was always lower than 1 m sec^{-1}.
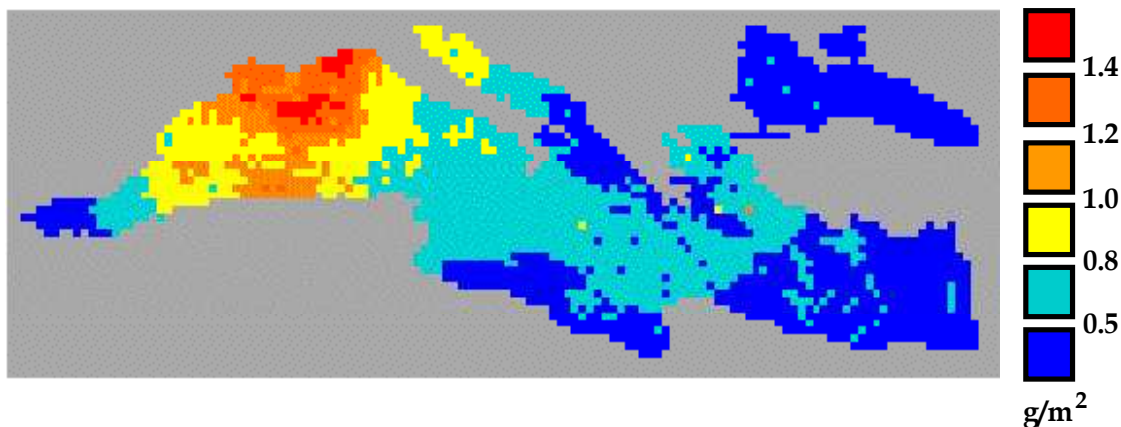

Fig. 4.1 - Meteosat-derived weekly maps of dust input to Mediterranean between July 27 and August 2 1983. Continuous input of African dust occurred during this period, peaking on July 30 1983. No significant rain was reported during this period. Meteosat daily images allow estimation of dry deposition flux (DULAC *et al.*, 1996) and geographical distribution is also shown. Corresponding dissolved phosphorus input ranges from 5 to 10 μg l^{-1} for NW Mediterranean surface waters.

Assuming 1.5 g m^{-2} of dust, 0.23% of P in the dust (GRAHAM and DUCE, 1982) and a solubility of 8% (LEPPLE, 1971), produces a flux of 9 μMP m^{-2} during this episode. This corresponds to an addition of 9 nM l^{-1} to a 1-m deep layer. This seems too small to produce a bloom (even assuming surface water P values as low as 20 nM). However, we do not really know how much P dissolved from the dust, so the flux may have been larger than the calculations suggest. Another point is that an input into a highly stratified layer would be more significant . While observations show a biological response after the dust storm, at this stage we do not know what the causal relationship was.

4.2 Wet deposition of dust: the role of Fe speciation in phytoplankton blooms

The *Cemiliania theory* put forward by SAYDAM (1996) suggests that the wet deposition of reduced iron from desert dusts to surface waters of the MED, during the day, has the potential to induce

phytoplankton blooms. Blooms have been observed several times in the Mediterranean and even in enclosed basins like the Black Sea, and have been linked with prior wet dust deposition events (SAYDAM and YILMAZ, 1998; SAYDAM and POLAT, in press).
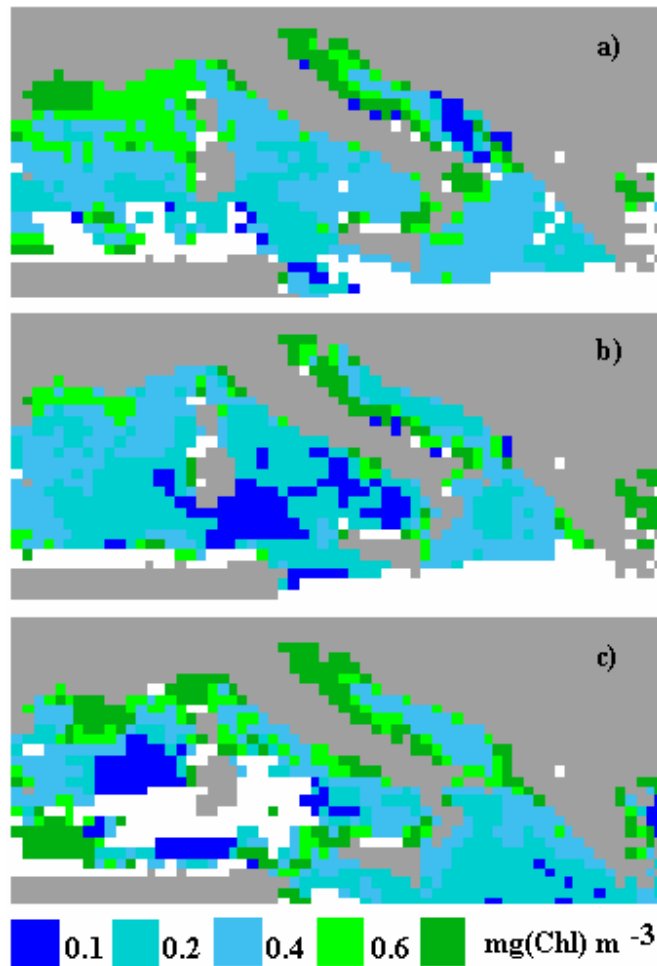

Fig. 4.2 - CZCS-derived weekly maps of phytoplankton concentrations during summer 1983: a) mid-June: spring blooms ended, and Ligurian and Adriatic Seas remained relatively productive; b) early August: during dust deposition event, whole basin exhibited low phytoplankton concentrations, except for coastal zone of Adriatic Sea; c) mid-August: 2 weeks after dust deposition event, unusually high concentrations were observed in Ligurian and Adriatic Seas.

An example occurred during the summer of 1997 over the Central Mediterranean and off the coast of Libya. AVHRR and Meteosat scenes from the period 1-2 June 1997 (F. DULAC, pers. comm.) indicate the transport and possible wet deposition of dust during midday over a position where a subsequent *Emiliania huxleii* bloom was later observed (Fig 4.4). Synoptic scale meteorological charts also confirm the presence of atmospheric vertical migration and a cold front over the region, supporting the view that wet deposition occurred.
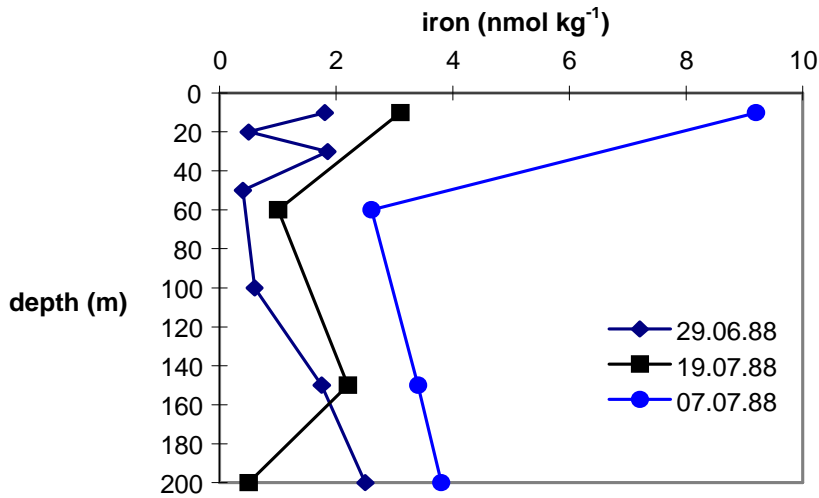
iron (nmol kg^{-1})

Fig. 4.3 - Vertical profile of particulate iron in surface waters of Ligurian Sea, before and after a major atmospheric input of Saharan dust on July 7 1988 (from DULAC *et al.*, 1996).

The *Cemiliania* theory necessitates the presence of "desert-originated dust" for the production of reduced Fe. Laboratory experiments of light-induced dissolution of hematite, goethite and lepidocrosite (SULZBERGER, 1993; SULZBERGER and LAUBSCHER, 1995) with oxalate as reductant ligand have shown that, at pH=3, only photochemical formation of dissolved Fe(II) occurs with lepidocrosite, but does not result in appreciable amounts of dissolved Fe(II) when hematite or goethite are used. In confirmation, the revised rainwater sampling strategy of OZSOY (1998) has shown that iron originating from desert sources may be photochemically reduced within cloud droplets to the +2 oxidation state, as suggested by FAUST (1994).

The importance of atmospheric sources in supplying iron to the surface of the open ocean is the subject of some debate. JOHNSON *et al. (*1997) showed that dissolved iron profiles in the Pacific and Atlantic Oceans have a uniform shape, with a 'nutrient-type' profile. They agree that the major source of iron to the deep sea is eolian transport, but show that integrated (surface to 500 m) concentrations are only poorly correlated with eolian iron deposition flux. However, BOYLE (1997) argues that the distribution of iron in deep waters is not well understood, and that the supply of iron to the open ocean is, in fact, predominantly eolian. Evidence of the impact of atmospheric inputs to particulate Fe levels in the MED may be seen in the distributions presented by DULAC *et al. (*1996). In that work, a dramatic increase in surface water particulate Fe was seen in the Ligurian Sea after a major input of Saharan dust in July 1988 (Fig. 4.3).

Despite the clear impact that atmospheric dust may have on particulate and even dissolved Fe loads in the MED (see section 2.6), it seems unlikely that Fe will limit biological production in this region, since dissolved Fe levels appear to be relatively high (>1 nM) and macronutrient levels are low. The possibility that it is the deposition of reduced Fe which triggers such events also seems unlikely, since
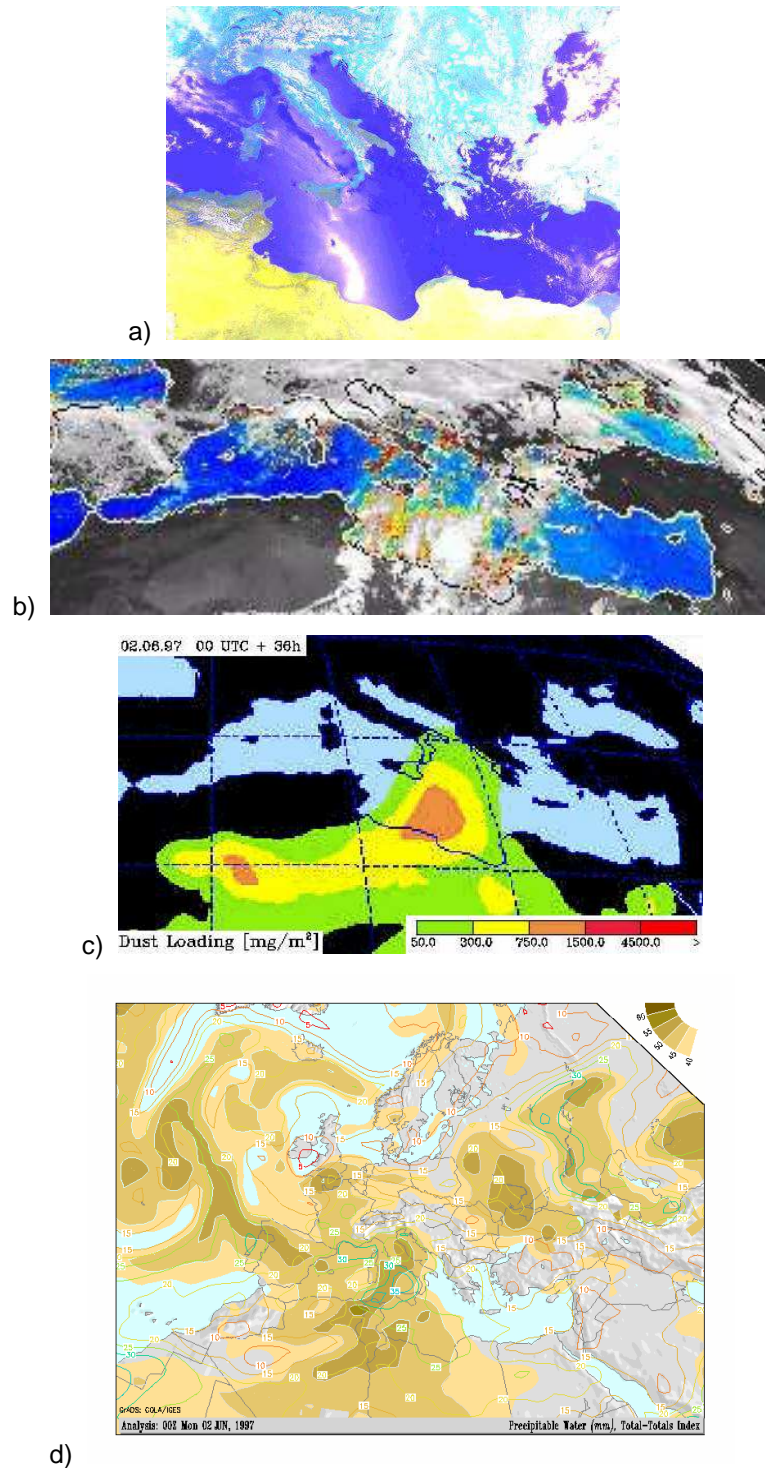
a)

b)

c)

d)

Fig. 4.4 - Four images representing respectively (from top): (a) NOAA-AVHRR composite imagery (June 9 1997), illustrating the high reflection region; (b) ADEOS Hearth Observation Probe UV-absorbing aerosol optical thickness imagery showing the massive dust outbreak over the Sahara and small filaments extending towards the Gulf of Sirte (June 2 1997); (c) dust loading prediction (June 2 1997) from MEDUSE model (*http://halo.hi.is/meduse/index.html*); and (d) possible wet deposition (June 2 1997) over a vast area offshore Libya, as derived from NOAA-AVHRR composite imagery (VIS and IR). Dust outbreaks in satellite image and deposition model was delivered to sea with rain, and may have triggered *Emiliania huxleii* bloom observed one week later.

photochemical reduction of existing surface dissolved iron during daylight hours, as proposed by JOHNSON *et al. (*1994), would already ensure a sufficient supply.

In order to evaluate this postulated relationship between atmospheric/oceanographic forcing functions and biological responses, it is important to establish whether the links are causal. This needs to be done through direct sampling of ocean and the atmosphere, during a strong Saharan dust event and the following weeks.

5. Conclusions

- Average atmospherically deposited annual mass fluxes of dust are estimated at 8-12-35 g m^{-2}, in the Western Mediterranean (WMED), Central Mediterranean (CMED) and Eastern Mediterranean (EMED) respectively. These fluxes are one-third those of riverine sources.
- Available satellite estimates agree well with the few offshore trap measurements.
- Atmospheric dust deposition is the most important part of the geochemical cycles for some elements (e.g. Pb, Cd, PAH).
- Saharan dust pulses not only perturb the atmospheric conditions above the Mediterranean but, following deposition of this material to the sea surface, they may have a significant effect on the concentration levels of some trace elements in the mixed layer.
- The speciation signatures of some trace metals are different in anthropogenic-rich (European) and crust-rich (Saharan) aerosols; in particular, more of the total concentrations of Cu, Pb and Zn are in exchangeable (potentially mobile) association in the anthropogenic-rich aerosols.
- Atmospherically-transported trace metals are transmitted to marine biogeochemical cycles following the deposition of aerosols at the sea surface by either 'wet' or 'dry' deposition. In both deposition modes, the solubility of the trace metals is constrained by the extent to which they are in exchangeable association in the parent aerosols; but, for the 'wet' deposition, solution pH and particulate load both impose additional controls.
- The importance of atmospheric input of nutrients to the Mediterranean increases from the shoreline to the open sea with the decreasing influence of riverine inputs, and from active mixing zones (margin "upwellings", frontal zones) to oligotrophic "stable" zones. On an annual scale, the nitrogen atmospheric input is significant for oligotrophic zones, where it may account for up to 60% of new production, whereas atmospheric phosphorus may only account for a maximum of 25%.
- Biological effects linked with wet and dry atmospheric inputs of nutrients are suggested.

5.1 Future work

Unique information on the geographic source and tropospheric transport of particulate plumes is provided by satellite observations, and the recently launched ocean and multispectral sensors (OCTS, POLDER; SEAWIFS) will allow more extensive and precise monitoring.

In order to provide insight on the impact of dust events on the chemistry and climatology of an enclosed sea such as the Mediterranean, satellite observations should be:

a) coupled to independent source tracers, including air mass trajectories and chemical tracers such as Sr, Nd and Pb isotopes, and

b) associated with nutrient and trace metal measurements at the onset and during specific events.

Certain specific actions are also recommended (CIESM, 1997):

c) expansion of the present rain/dust collection network in the EMED and SMED regions, to provide more complete regional coverage of dust deposition of the basin;

d) a well-coordinated multidisciplinary research effort should be planned aimed at sampling the atmosphere and the surface MED in real time during and immediately after a Saharan dust event, to take advantage of this natural seeding experiment.

e) a data base should be established, to file existing atmospheric and oceanic information in the Mediterranean; this data base should be available to all workers in the field and could be supported by an international commission such as CIESM (Commission Internationale pour l'Exploration Scientifique de la mer Méditerranée).

6. Acknowledgements

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