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Input of various chemicals transported by Saharan dust and depositing at the sea surface in the Mediterranean sea

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Abstract

This paper reviews work on the role of Saharan dust as a contribution of various chemical to the Mediterranean basin. Both the magnitude and the mineralogical composition of atmospheric dust inputs indicate that eolian deposition is an important (50%) or even dominant (>80%) contribution to sediments in the offshore waters of the entire Mediterranean basin. The Mediterranean Sea is a semi-enclosed basin, that receives substances sporadically from the arid region of the Sahara desert. We considered the location and strength of source areas, the transport paths of material away from the desert, the number of Saharan dust transports per year, the way to be dust is deposited (wet and dry mode), the fluxes of Saharan dust, the nature of the material, and the contribution of nutrients to the sea surface. Estimates of atmospheric inputs to the Mediterranean and some coastal areas are reviewed. Model data for nutrients indicate that the atmosphere delivers the nitrogen and one-third of total phosphorus to the entire basin. Measured data in sub-basins, such as the Western Mediterranean and Eastern Medieterranean indicate an even greater proportions of atmospheric versus riverine input. 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 depositionto overall production in the basin it has been suggested that certain episodic phytoplankton blooms are triggered by atmospheric deposition of N, P or Fe. Iron fluxes may be important in determining the nature and quantity of carbon fluxes from Fe-rich areas (like MED Sea), in addition to Fe-poor areas such as the extant Southern Ocean. A geophysiological model shows that iron removal from the photic zone does occur at a much higher rate than the conventional biological pump can account for and that this might release the risk of excessive phosphate scavenging.

Key Words *dust Sahara atmospheric transport Mediterranean Sea dry and wet deposition fluxes nutrients*

Introduction

Desert dust is a source of mineral aerosols, whose geological and biological implications are now recognised [1,2,3,4,5,6,7]. The climatic role of desert dust is an important question in the crucial debate on global change [8,9,10,11].

The biogeochemical impact of desert dust also remains a matter of discussion regarding its contribution for different major and minor elements to terrestrial and marine systems and especially its potential fertilizing role for remote oceanic areas by supplying micronutrients as phosphorus and iron [4,12,13].

In the Mediterranean (MED) many studies have described the occurrence of Saharan dust events, the mineralogical and chemical properties of Saharan dust, and emphasized its geological and biogeochemical roles [see e.g., [14,15,16,13].

Finally several modelling systems have been developed to predict the desert dust cycle in the atmosphere [17] and to derive the amounts of Saharan dust transported to the USA [18] and deposited on the MED Sea and Europe [19,20,18].

Transport from Sahara over the Mediterranean basin

Source areas of Saharan dust

Saharan dust is transported from its source areas northward across the Mediterranean (MED) [14,21] to southern Europe [22,23] and sometimes as far north as Scandinavia [24]; and along easterly trajectories across the eastern MED [25,26], to the Middle East [27]. A dust reservoir is continuously produced over the Sahara and transported across the desert margins. However the author [28] noticed no continuous flow of dust over the MED and Europe. Several distinct source areas are thought to be productive in the Sahara Desert. The importance of the various regions as a dust sources are relate to several factors. A high content of silt and clay size particles alone is not sufficient to characterise an active source area. Finally, metereological condition and surface roughness must allow for high wind speeds directly at the soil/sediment surface in order to entrain particles [29]. The papers [30 and 3] distinguish between nine different landscape units, which are potentially important sources for dust entrainment in arid and semi-arid areas; 1. dry wadi sediments, 2. dry lake sediments, 3. sebkhas, 4. alluvial fans, 5. loeass areas without vegetation, 6.

clayey sediments, 7. former stabilised, now remobilised sand dunes, 8. stoney deserts with weathering rates and 9. exposed regolith and paleosoils. The landscape units listed above cover a different surface area, with different concentrations of particles susceptible for long range transport, and a different erodibility. However, Saharan dust is derived from arid soils, alluvial fans, which do not exhibit the same composition as the global upper crust. As chemical fractionation occurs during weathering processes, mean surface soils or detrital silts and clays are already different from the mean crustal material [31,32].

The precise dust-source locations in the Sahara region is a subject of controversial discussions in the literature. This is because the geomorphology of the Sahara is rather complex, comprising rock deserts, gravely soils, loamy soils, salt desert, sandy desert and a mixture of these different types. The author [28] attempted to review previous studies of Saharan dust sources, but found results totally different. A number of source identification methods have been used by different workers, starting from: back trajectory analysis, isobar data, use of mineral tracers, remote sensing and analysis of surface dust observations. The paper [33] showed that dust transport across the northern borders of the Sahara into the Western MED and southern Europe is more frequent, mainly originated from Marocco-Western Sahara, Mauritania (A1); south Algeria, Mali and west Niger (A2). Avila and co-workers [22] and Molinaroli [34] traced deposition events back to three main areas: Western Sahara, the Moroccan Atlas, and central and south Algeria. Yaalon and Ganor [35] calculated that a consistent dust flow is “channelled” from the Sahara over the EMED both from south Libya, east Niger and Chad (A3); south Egypt and north Sudan source (A4) [35] (Fig. 1).

It is been calculated that source A1, A2 and A3 have a dust production of over 200 million of tons per year. Dust production from source A4 is relatively weak. The transport of dust from the Saharan and Sahel regions takes place throughout the year, but is particularly strong between March and June. The transport direction is determined by the general circulation pattern.

In recent time the source areas have been identified by METEOSAT (measurements of infra-red radiances). Legrand [36] stated three sources in front of the MED (M1-M3); M1 covers most of the Atlas mountain chain and its sediments in Marocco and NW Algeria. M2 comprises areas in Algeria, Tunisia and Libya. Both are sources for dust transports across the Western Mediterranean (WMED). M3, located in NW-Egypt is the dust source for Eastern Mediterranean (EMED). Two other sources in central to southern Saharan and Sahelian areas (S1-S2) were identified. S1 covers the Bodélé depression located between Tibesti and Lake Chad. Both are responsible for dust transport towards the Atlantic Ocean.

D’Almeida [33] estimated a total mass production of approximately 700 million tons; about 60% of the mass moves southward to the Gulf of Guinea and less than 30% are transported across the

northern equatorial Atlantic Ocean to the Caribbean Sea. Dust transport across the northern borders of the Sahara into the MED is approximately 12% of the total, i.e. ~ 100 million tons (~ 13 of which are < 5 μm). These estimates are subject to severe uncertainties in relation to large-scale meteorological features (dry years, ITCZ latitudinal position) which determine strong interannual variabilities. While most of the indirect measurements (model, METEOSAT, AVHRR) show that the transport peaks in summer [37,38,39] the direct measurements [40,41] and the historical inventories of occurrence of dust rain or dust haze in Europe (e.g. [42]) indicate maximum fallout in spring and autumn. Transport from North Africa to the EMED occurs predominantly during spring and is commonly associated with the eastward passage of frontal low-pressure systems. Dust from sources in the Middle East is more typically transported to the MED in autumn [43,26]. Analysis of 23 heavy dustfalls in Israel over a 20-year-period suggest that the North African type is by far the most common [44]. South Algeria is the most frequent source area for Saharan dust, reaching Israel. Ganor and co-workers [44] (1991), and Ganor and Foner [45] distinguish between material commonly transported from sources in the Hoggar Massif and the Tibesti mountains in Northern Chad, the latter also picking up material from the Western and Sinai Deserts.

Figure 1

Atmospheric deposition: dry and wet modes

From Saharan deposition studies in the WMED, it is apparent that different seasonal cycles must be taken into account when considering both wet and dry patterns. Guerzoni and co-workers [46] showed that continuous analyses of dry and wet deposition in Sardinia, the most southerly station available in the WMED, demonstrated that approximately three-quarters of the Saharan dust is deposited with precipitation. This result has been documented in Corsica [47, 48]. For the aerosols, a simple model was presented in [49], where it was shown that crust-enriched aerosol concentrations are latitudinally controlled. If aerosol values (and associated dry deposition) are generally higher during the hot season, the transfer to the ground is more significant in spring and autumn.

Guerzoni and co-workers [21] presented average concentrations of mineral dust in air (MSP) and particles in rain (TPC) in Sardinia (Italy), subdividing the samples into “background” (non-Saharan) and “Saharan” (Tab. 1). The table shows that approximately two-thirds of the dry, and half of the rain, episodes sampled did not include a Saharan contribution. The MSP data confirm previous work, that shows average background dust concentrations in the western MED between 2 and 4

µgm^{-3} [47,1,50]. They also identified crust-enriched group representing samples with some crustal enrichment of Saharan provenance, mixed with other contributions often not identified. The aerosols in this group have MSP values twice the background values, and the rain samples have pH values between 5.6 and 6.0. The Saharan group also highlights the "outbreaks", i.e. the biggest direct transport events. The number of crust-enriched episodes reported by the same authors (40 year^{-1}) is higher than that found in Corsica by Bergametti and co-workers [47] (1989a) of 20 events year^{-1}, whilst the two strong episodes of Saharan dust outbreaks agree with the 2-4 outbreaks recorded yearly [51]. The authors [23] described an occurrence of 4-7 episodes of Saharan intrusion in NE Spain up to 10-23 annual events in the Southern part of the country.
Total particulate content values (TPC) are also highly variable, with half of the samples classified as background (GM < 1 mg l^{-1}) and two red dusts with the highest TPC content (GM = 263 mg 1^{-l}). The atmospheric annual deposition of particles measured in Sardinia was 1100 µg cm^{-2} (250 µg cm^{-2} dry and 850 µg cm^{-2} wet).

Table 1

Dust storms over Israel are usually associated with a cold front with a significant downward flowing jet stream and are often accompanied by rain [52]. Long-range transport of Saharan dust to the Central Mediterranean (CMED) is characterised by events lasting 2–4 days, compared to an average duration of just 1 day for events reaching the EMED from the Arabian Desert [53]. Most episodes occur in March and April (and to lesser extent, in May). Over the 33 years that measurements were taken, there appeared to be an increase in the annual number of dust episodes over the EMED - possibly related to global climatic changes [45]. The number of Saharan dust transports was estimated in 10-12 year^{-1} [35]. The authors [26] showed that during 1992 only two events transported ~ 30% of the annual atmospheric deposition. In the years 1978-1990 there were more dust episodes than in the period 1958-1976. The number of annual dust episodes varied between 5 and 35, averaging 19.
A database has been developed in the framework of the Seasonal, INterannual and decAdal variability of the atmosPhere, oceanS and related marIne ecosystems (SINAPSI) project, to provide an estimate of the occurrence of Saharan dust events over the MED and an estimate of the temporal and spatial variability in the atmospheric forcing (dust events) and in the marine ecosystem response.
The collection of data and imagines of dust events was possible to be part of a mailing list organised by J. Prospero of the RASMAS, University of Miami. The Dataset contain The Sea-viewing Wide-Field-of-View Sensor (SeaWiFS) true color and TOMS images from 1998 up to 2003 [54]. The

images are available on the internet: http://www.nrlmry.navy.mil/aerosol/ ; http://seawifs.gsfc.nasa.gov/SEAWIFS/HTML/dust.html; and http://www.osei.noaa.gov/Events/Dust/. The information retrieved by the cataloguing concerns space-time distribution of dust throughout the years examined. Sciarra and co-workers [55] developed a similar database for the year 1998-2002, they also provided an estimate of seasonal occurrence of Saharan dust events and the total amount of dust. The results showed different number of days of dust each year. The years 1998, 2000 and 2002 were quite similar. They authors counted a mean of 94 days of dust. On the contrary, in the years 1999 and 2001 a larger number of "dusty" days were counted, 124 and 146 respectively. These two years cannot be considered as "anomalies" because of the limited data set.

Mineral particle fluxes

Several theoretical problems delay 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 [4].

Figure 2 and table 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 MED. 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 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 (see direct measurement in [56]), mass fluxes were recalculated using an SR of 500, and are listed in table 2. When SR=500 is used, the two estimates agree very well.

Figure 2

Table 2

With the data from table 2 the mean values of 8, 12 and 35 g m^{-2} yr^{-1} for WMED, CMED and EMED respectively were calculated, these values were used to estimate the total annual

atmospheric dust flux, which turned out to be ~40x10^6 tons for the whole MED basin (Table 3) [16].

Table 3

The authors [21] calculated the monthly dry flux data, as sums of ten 3-day aerosol samples, and the monthly wet fluxes, were both calculated for the period October 1990-April 1991 and May-October 1992 in Sardinia.

The wet mode prevails largely over the dry one, and that a few episodes account for most of the particles fluxes. Particulate fluxes in Sardinia show a marked annual variability; 581 µg cm^{-2} for one wet episode accounting for more than 60% of the total annual flux in 1990/l991. Le Bolloch and Guerzoni [40] have shown that the same occurred in Sardinia in another period (1992/1993), where 208 µg cm^{-2} for three events accounted for 80% of the flux, even though a decrease in the wet flux was noted for this year. A more long-term record, such as that of [42] shows that both present fluxes and the dust fallout peak in February/March and October/ November, are in close correlation with the wet seasons. Very low deposition rates are recorded during the summer; apart from the scarcity of precipitation during this period in the MED, several reasons seem to prevent high deposition in summer, despite the high emission frequencies, including (i) the gradient between warm air and cold fronts, usually associated with outbreaks [64] and (ii) upward dust movement, which determines much lower real dust deposition than expected by grain-size data and model calculations [38].

In the work [21] the authors found that the wet components provided more than 70% of the total wet flux in a single episode. Loÿe-Pilot and co-workers [48] found a similar pattern in Corsica, with several episodes accounting for 20-70% of the annual particle flux. Estimates of rates of dust deposition exist for a number of sites at varying distances from the Sahara source area (Tab. 4).

As might be expected, there is a tendency for rates to be lowest at large distances from potential sources. Thus the values for Western Europe (e.g.. Central France and the Alps are less than 1 g m^{-2}.

Further south, in NE Spain, a value of 5.1 g m^{-2} is recorded, while over Sardinia, Corsica, Crete and the SE MED, most values are between 10 and 40 g m^{-2}. Average of the dust fluxes in the EMED are between 30-60 µg m^{-3}, but they can increase up to 150-1500 µg m^{-3} during sand dust storms [65]. However, given the absence of very long-term direct measurements of dust deposition over large areas, estimates of dust deposition have been gained by modelling [19], using dust concentration data. The model indicates deposition rates for the Mediterranean of 3–14 g m^{-2} yr^{-1}, which are comparable to those obtained from direct measurements [21]. Much lower model-derived data were

recently presented in [18], with deposition rates ranging from ~1 to ~3 g m^{-2} yr^{-1}, by using SKIRON/Eta model. The reason could be the use of an average dust particle diameter of 2 µm, that may led to an underestimation of the total mass dust deposited (see below for grain size data). However the use of numerical model and the analyses of ground- and satellite-based observations are essential to have a feeling of the magnitude and the geographical distribution of the dust deposition in absence of direct measurements. The SKIRON/Eta modelling system is in operational use [17] and provide 72 hours forecast for the Mediterranean region and the results are available on the internet (http://www.icod.org,mt and http://forecast.uoa.gr).

Table 4

Saharan mineral dust input and properties

Volume particle-size distribution

The particle size distributions of Saharan dust are summarised in Table 5. Data in the table represent dust storms which have travelled outwards into the moister parts of West Africa, to MED or to Europe. It is possible, therefore, that dust storms from near the source will have coarser grain size characteristics than those listed. The mean, mode and median size data provide little information about the maximum sizes of grain that can be transported in dust storms derived from the Sahara. Molinaroli and co-workers [49] observed that dust particle diameters during Saharan dry transport consist mainly of silty-clay or clayey-silts, with particle size diameters ranging from 0.5 to 60 µm in CMED. The authors also showed a bimodal structure the two modes were between 3-4 µm and 50 µm in diameter. Such a structure has been shown by D'Almeida and Schütz [72], to be characteristic of aerosols from the Sahara. Particle size distribution of Saharan wet transport collected at the Sardinia stations showed modes at 8 µm for the first and a single mode between 20 and 40 µm for the second. It is apparent that the wet aerosol was enriched in large particles compared to dry aerosol dust. It therefore seems reasonable to attribute differences in the size distributions of the Saharan dust to different transport and deposition (dry and wet) modes, which, in turn, are related to different transport velocities and lengths of airborne trajectories.

Table 5

To better evaluate and characterise the Saharan dust in the MED area, distinct episodes of Saharan dust (dry and wet) are reported for different land-based stations. It must be emphasised that the data

from the authors were collected at different times and with different methods and thus cannot be directly compared. Guerzoni and co-workers [80] measured mass particle size distributions from rain and aerosol Saharan dust in Sardinia; the median was about 15 μm in two different rain samples with the presence of two modes (3 and 15 μm) in one aerosol sample. In the paper [81] were measured particle size distribution of a Saharan dust collected in precipitation in the northern Pyrenees (France). The dust particle diameters ranged from about 1 μm to 100 μm, with a median volume diameter of 8 μm and a maximum concentration at about 10 μm. The work [82] reported the results of several Saharan deposition events (dry) in West Germany with a very high variability of the median diameter between 2.2 and 16.1 μm. Tschiersch and co-workers [83] measured a volume size distribution of Saharan dust in snow from the Jungfraujoch (3450 m above sea level), Switzerland. They showed particle size distribution between 1 and 4 pm, with a mode at about 4 μm. A decrease of the mean diameter of Al from - 4 pm to - 2 μm, during the transport of mineral aerosol from Africa over the MED Sea was also observed [84].

In conclusion, the particle size distribution in the Saharan dust exhibits no clear relationship between median, or modal particle size and transport distance. With respect to long-range transport, grain size fractionation is not a clear function of aerosol sedimentation velocity, and factors other than gravitation and turbulence may play an important role. Nevertheless, the presence of giant particles is common and explains the wide range of deposition velocities associated with desert-rich aerosols found by different authors. Saharan dust collected after numerous fallout events over the British Isles has shown that large numbers of so called ‘giant’ dust particles (> 62.5 μm) are commonly carried more than 3000 km to Northern Europe [85].

Mineralogical composition

The papers [14, 21] have shown the relationship between eolian deposition and sedimentation in MED basin. They found that the atmosphere contributes on average from 10 to 30% of recent sediments. Here, we highlight the possible role of mineralogy in identifying the contribution of atmospheric input to the MED basin.

The mineralogical signature may be used as an indicator of dust source. 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. Clay minerals have the potential to act as “source tracers” for material transported into the MED basin. There are now available a large number of

studies of the clay mineralogy of Saharan dust and these show major geographical variations in the proportions of different clay minerals derived from different source areas.

For example, palygorskite has been used as an indicator of dusts originate of Western Sahara, northern Algeria, South of Hoggar and in the Tanezrouft [86] in samples collected over WMED and CMED [87,88,34].

Another approach is to look for mineral associations which are characteristic of any particular weathering regime, whereas kaolinite, which may also be produced in a variety of weathering conditions, is characteristic of desert weathering system. Dust samples collected from the Northern Nigeria displayed a predominance of kaolinite [89,90,91] McTainsh and Walker, 1982). Dust in the North and Central Sahara are high in carbonate contents up to 20–50% and the dominant clay minerals are illite, chlorite, palygorskite and montmorillonite. In the paper [92] were identified four different groups or sectors along a transect in the Sahara from 19–35°N. In Northern Algeria, illite accounted for around 70–75% of the clay content, kaolinite about 15% and palygorskite 10–15%. Around Tamanrassett, Tessalit (Mali), illite-chlorite were dominant ~60%, palygorskite was 5–10% and kaolinite 25–30%. South of Hoggar and in the Tanezrouft smectites were dominant, followed by kaolinite 20–25%, illite 10–25%, palygorskite 10–15% [93].

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 (Table 6). In the CMED mixed dusts are observed. Smectite is very common in the EMED but not in the WMED. Caquineau and co-workers [94] identified the illite/kaolinite ratio as an crucial tracer for the African source dust to the MED (Table. 6). They observed a range of I/K values from 2.4 to 1.6 in north-west Africa. WMED dust transported from the Sahara originating from north-west Africa shows an I/K ratio of 1.8.

Table 6

The CMED has an average I/K ratio of 4.0, this very high ratio presumably shows that the dust is a mixture of Saharan and background dusts (European). The EMED has a low I/K ratio (0.8). A relatively low I/K ratio (0.7) is associated with north east African sources.

Saharan dust and input of nutrients

Mineral fragments are relatively insoluble in surface ocean waters, and settle largely unaltered through the water column to be deposited in sediments on the sea floor. Accumulation of this material can influence biogeochemical cycles.

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 [97]. By aiding preservation, dust deposition can accelerate the removal of various chemical species (including nutrients and carbon) from the ocean, with consequences for ocean productivity and the global carbon cycle. 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 [98,99,100]. Once again, there is a more direct and powerful effect of dust deposition. The major nutrients required by the primary producers of the open ocean (phytoplankton) are phosphate (PO_4^{3-}), nitrate (NO_3^-). As phytoplankton cells grow and divide in the sunlit surface layer of the ocean (the 'euphotic zone'), nutrients are removed from solution and transformed into cellular constituents. Most of this material is ultimately broken down ('remineralised') by the action of bacteria and zooplankton within the euphotic zone, returning the nutrients into solution. A fraction (in the form of dead cells, zooplankton fecal pellets, and other particulate organic debris) escapes and settles through the water column under the influence of gravity, being remineralised much deeper in the ocean. Although nutrients are eventually returned to the euphotic zone by upwelling and mixing, a vertical gradient is created with lower nutrient concentrations at the surface than at depth.

Despite early observations of P limitation [101,102,103], recent works suggest that MED surface waters are nitrogen-limited [104,105]. In fact, there is growing evidence that the EMED is phosphorus-limited [106] and that the WMED is probably N-limited [107,108], or that limitation shifts from nitrogen to phosphorus and *vice versa* depending on the period of the year [101,109] or the area considered [110]. 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.

Saharan dust and nitrogen

If only particulate dry species are taken into account, nitrogen dry deposition represents 25–33% of wet deposition in the north-west basin [111,112]; 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 7, which also lists data from the UNEP Mediterranean Pollution (MED POL) Project (computed from models) for 1991 [113,114]. 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) [113], 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 [111].
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.

Table 7

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 [116,117]. The source of organic nitrogen is not known, but [116] believe that a large fraction of it is anthropogenic.
The few measurements of organic nitrogen content in the Mediterranean atmosphere [118,115] 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.
If the entire WMED is considered [111], 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 MED according to UNEP/WMO estimations [119], the atmospheric input being redominant in the southern zones. The atmospheric input is ~60% of the total continental supply of nitrogen to the Mediterranean [119].
Because 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.

Impact of atmospheric input of nitrogen on primary production

Atmospheric input of N contributes to new production [120,121,97], 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} [122,123] 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} [106]. In this case, the atmospheric input of nitrogen, 2.1 g C m^{-2} y^{-1} represents ~12% new production.

Saharan dust and phosphorus

Phosphorus values of Saharan dust range from 0.04% found in the SEMED to 0.07% from Libyan desert material [63]. Values as high as 0.25– 0.40% were found in Saharan dust collected in the NWMED [16]. 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 the work [106], Saharan dust may act as a trap for soluble phosphorus by adsorption of PO_4^{3-} on to Fe-rich particles, whereas [124] found that up to 8% of Saharan dust phosphorus is soluble in seawater. From a partitioning study between crustal and anthropogenic phosphorus, [125] 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% .

Table 8 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 9 shows inputs of nitrogen and phosphorous in the three sub-basins.

Table 8

Taking the two values from [125] and applying the Redfield ratio (C/P=106/1) gives potential carbon production as a result of 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, but 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 [63].

Table 9

Saharan dust and iron

Marine ecosystem appears to play a major role in CO_2 withdrawal from the atmosphere as a result of export production. On the other end primary production needs basic elements (nitrogen, phosphorus, silicon, iron etc.) to work. The mechanistic approach looks for the factor that ultimately regulates (limits) primary production in the ocean in different areas and ages. Since the author [128] explicitly proposed that iron could be the factor modulating CO_2 oscillations during glacial-interglacial periods a lot of effort has been invested to demonstrate that iron is, indeed, a basic regulator also in wide areas of the extant ocean.

Marginal seas are in general more exposed to terrestrial inputs, and iron supply to the ocean definitely relies on atmospheric transport from the land. Indeed, estimates of atmospheric inputs to the Mediterranean and some coastal areas were reviewed by [16], who also considered uncertainties in the estimates. The present day Saharan dust fluxes (~ 1 mg cm^{-2} yr^{-1}) account for about 10-20% of the recent deep-sea sedimentation in the WMED. In particular, minerals involved in the processes are calcite and dolomite, with solubility ranges from 10 to 80%, that led to an yearly Ca atmospheric flux -due to Saharan contribution- of approximately 50- 200 mg cm^{-2} yr^{-1}. In the case of Fe, iron oxides (hematite) and oxyhydroxides (goethite) are the minerals involved, with lower solubility range (from 5 to 20%) and associated yearly fluxes of 300-600 mg m^{-2} yr^{-1} (i.e., 20-40 µmol Fe m^{-2} d^{-1}).

Their conclusion was that, in spite of the apparently small contribution of atmospheric deposition to overall production in the basin, certain episodic phytoplankton blooms could be triggered by atmospheric deposition of N, P or Fe. Moreover they reported evidence of a presumably coccolithophore bloom approximately a week after the dust deposition and speculated that a cause-effect relationship could be inferred among the two events. In fact, whether there is a connection between Saharan input and *E. huxley* or other coccolithophore blooms, it could be tested by investigating the presence and variation of coccolith and biomarkers in marine cores, and their connections with climate-related parameters. Apparently a larger uncertainty on CO_2 concentration control is associated with interglacial periods. Some other interesting results came by investigating the possibility of using iron minerals in marine core samples as a proxy for past (Holocene/glacial)

dispersal of aeolian sediments from North Africa [129]. The data suggested that aeolian transport had varied both temporally and geographically.

Guieu and co-workers [130] showed interesting results about the total atmospheric input of iron measured in Corsica over a period of 2 years. The iron flux of Saharan origin was recalculated for the samples collected over the period and the proportion of iron of non-Saharan origin varied from 0 to 16% with an average of 4% over the period, indicating that the atmospheric deposition of Fe is entirely dominated by Saharan inputs, anthropogenic inputs being minor. Iron is an essential nutrient for phytoplankton growth [131]. The question of the dissolution of atmospheric iron in seawater is important as dissolved Fe could be, in some stratified situations, a limiting factor for phytoplankton growth. Taking into account several field studies, [59] proposed that the dissolved flux represented 4–17% of the total atmospheric flux of iron. It should be noted that in this budget the atmospheric flux of total iron used was the lowest recorded over the past decade. The annual flux measured at the in Corsica in 1995–1997 was lower by a factor of 4–6 compared to the one measured in 1987 [132] when high dust fluxes were recorded in Corsica [41]. This indicates that during the period 1986-1989 high dust flux the budget of dissolved iron was even more dominated by the atmospheric inputs of Saharan origin. Atmospheric inputs from Sahara its probably the controller of the budget of total and dissolved iron and thus the potential biological impact of iron in the western Mediterranean [130]. In the absence of any Saharan event or during the summer stratification, as a first approximation, the previous authors hypothesize that almost no iron is supplied to the mixed layer (although this may be overstated in particular after a strong wind event as mixing with deeper water may occur). In this case, dissolved Fe concentrations should be very low at the surface, which was confirmed by the values <0.13 nM observed in the NWMED in May during a period of phytoplankton bloom [133].

Volpe and co-workers [134] processed SeaWiFS data relative to the year 2000 to obtain atmospheric and oceanic parameters to monitor Saharan dust events and ocean phytoplankton blooms on daily basis. They also applied the SKIRON model outputs to localize the Saharan dust deposition area of each event in order to evaluate the biological impact by observing the evolution of the SeaWiFS images and to estimate the time response of phytoplankton to atmospheric nutrient inputs. The results showed that 93 events occurred in the MED in the year 2000. The analysis of the chlorophyll time series in correspondence to the dust wet deposition showed that the atmospheric contribution seems to have some influence on the productivity of the MED basin (Fig. 3). Furthermore, the atmospheric nutrient deposition gives some evident signal in enhancing biological activity.

Figure 3

The cause-effect relationship between nutrient bursts and plankton growth is among the basic paradigms of biological oceanography and is rooted on repetitive studies on upwelling systems. Certainly, less is known about what species would take the advantage and why and, more important, if any competition would arise among different groups. A geophysiological model for the Mediterranean water column was presented by [135], where a possible link between climate, "fertilisation" of certain phytoplankton groups by North Africa desert-derived inputs and the resulting water column biogeochemistry was explored. This was related to previous papers suggesting that nutrient inputs, and particularly iron, from Sahara desert could affect the biogeochemistry of the Mediterranean Sea [130,136,137]. The proposed mechanism suggested an opposite, while not contradictory, point of view of iron effect on marine production, *i.e.* that the euphotic zone may experience (dust-induced) fluxes far in excess of biological requirements. The reactive components of this Fe flux may complex with and remove dissolved P, thereby affecting the ocean N:P ratios which are thought to be important in determining phytoplankton ecology.

Effects of atmospheric input on surface sea biogeochemistry: a geophysiological model

In the paper [135] a dynamic one-dimensional water-column model is presented in order to explore the feasibility of biogenic carbonate as an iron sink. It was based on [138] photosynthesis, simple light attenuation, Redfield stoichiometry in phytoplankton, [139] respiration, dispersion coefficients and initial nutrient concentrations from [140] and the input atmospheric fluxes shown in figure 4.

Figure 4

The phytoplankton populations grow and respire, consuming and 'respiring' nutrients, until either P, N or Fe become limiting, at which point excess C fixation is channelled into either exudates (diatoms) or carbonate (coccolithophorids) (see figure 4 in [135]).
The exudates generate flocs which settle rapidly through the water column and produce sub-oxic micro-environments within which net denitrification occurs. The carbonate traps Fe-PO_4 complexes, liberating the PO_4 and exporting the Fe.

Although hypothetical, these mechanisms addressed an important geophysiological question: how do inter-species competition and environmental self-organisation become coupled? The authors have approached this question on the basis that competition for a limiting resource (in this case P) may occur via species-specific responses (in this case excess C products) that result in limiting the availability of other resources (in this case N and Fe). This results in a system with a tendency to converge on a state of balanced limitation, integrating species dependence and competition, using ecological succession as its mechanism. The key processes with respect to this model are therefore species-specific Fe and N export.

Mass balance (Fig. 4) shows that N fluxes, as with Fe fluxes, require a sink in excess of the equivalent P. Although atmospheric input N:P and deep water N:P show ratios of between 20 and 25, the euphotic zone is not enriched in N, and often N limited at the top and P limited at the bottom [140]. There are two candidates for the surficial N depletion; high N:P in organic matter export or net denitrification. Their initial model runs have used constant Redfield ratio organic matter with no differential N and P respiration, hence they have used denitrification to export N excesses and provide a competitive basis for diatoms.

The model was run firstly to explore the effect of the phytoplankton strategies on their resultant populations. The results are shown in figure 5. In the absence of both carbonate and exudate formation, rapid growth during the first few days of simulation results in a stationary phase total biomass.

Figure 5

With only diatom exudation and no carbonate production, this stationary phase biomass is 9 % lower due to N depletion. With only coccolithophorid carbonate production, the stationary phase biomass is 18 % higher due to greater P availability. In the presence of both carbonate and exudates production, the total biomass shows a marginal increase to 21 % higher.

Secondly, the model was run with a varying atmospheric input of Fe, whilst N and P fluxes were kept constant. The results are shown in figure 6. The model shows maximum biomass at MED iron fluxes (30-60 μmol m^{-2} d^{-1}), and less when Fe fluxes are lower or higher. Org- and CO_3-C fluxes where measured at 100 m depth after 50 days of simulation.

The very high CO_3 fluxes (10-30 mg C m^{-2} d^{-1}) are partly due to nil CO_3 consumption, representing a massive flux of carbon in the euphotic zone (EZ). The reason so much is produced is because the diatoms tend to grow at the bottom of the EZ, leaving the top dominated by coccolithophorides. At the top there is a lot of light and very little nutrients (mostly atmospheric), hence lot of excess carbon. Thus the model is able to reproduce the partitioning of EZ with the top of it changing its

depth in relation to the atmospheric flux of nutrients relative the flux of nutrients diffusing from below.

Figure 6

In the model the organic-C and carbonate-C fluxes were inversely proportional, partly because high coccolithophorids means generally low biomass and partly because in the model coccolithophorids do not make aggregates hence the settling rate is lower. However when Fe fluxes are higher than 40-60 µmol m^{-2} d^{-1} (Fig. 6) the system shifts from the main trend producing another trend where approximately three times more carbonate is exported per org-C exported.

Conclusions

Average atmospherically deposited annual mass fluxes of dust are estimated between 8 and 35 g m^{-2}, from the WMED, to EMED. These fluxes are one third those of riverine sources. Other estimates -based on models- give deposition values of 3 to 10 times lower than those obtained by measurements.

Several locations of Saharan dust source areas have been identified combining different methodologies (e.g., back trajectory analysis, isobar data, use of mineral tracers, remote sensing and analysis of surface dust observations data). The mineralogical signature may be used as an indicator of dust source. Mineral dust mainly consists of a mixture of silicates (clay minerals, feldspar, quartz) associated with carbonates, and the abundance of each of these minerals in dust is highly variable, mainly reflecting the source composition and its evolution during transport.

The wet and dry mode particle size distributions of Saharan outbreaks collected throughout the MED range from 0.5 to 60 µm. A bimodal structure is often observed for the dry and wet mode. Individual episodes of total Saharan dust (i.e. wet +dry deposition) at different land-based stations in Europe exhibit no clear relationship between median particle size, modality and transport distance from the primary desert source. Trajectories of long-distance transport are relatively well documented, and confirmed by the TOMS data

Comparing data obtained in the MED with a number of Saharan dust parameters no clear latitudinal patterns emerge for the overall deposition of Saharan dust. The wet deposition that dominates the flux of Saharan dust to the MED Sea is controlled by the frequency of precipitation rather than atmospheric concentrations of Saharan dust. However, this overall control can be modified by the input of Saharan dust pulses, which can result in dry deposition exceeding wet deposition at certain

times. The annual dust flux can be controlled by a few episodes of Saharan outbreaks; sometimes a single outbreak can account for more than 50% of the total annual Saharan dust flux. Satellite observations in the period 1998-2002 shown an interannual variability in both the frequency and the amount of dust involved in the events.

Saharan dust has important influences on nutrient dynamics and biogeochemical cycling in oceanic ecosystems in the MED Sea. The importance of atmospheric input of nutrients to the Mediterranean increases from the shoreline to the open sea, 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 Fe were also suggested. Iron fluxes may be important in determining the nature and quantity of carbon fluxes from Fe-rich areas (like MED Sea), in addition to Fe-poor areas such as the extant Southern Ocean. A geophysiological model shows that iron removal from the photic zone does occur at a much higher rate than the conventional biological pump can account for and that this might release the risk of excessive phosphate scavenging.

Atmospheric dust concentrations may therefore have considerable climatic significance through a range of possible mechanisms, and the frequency of dust events can change substantially in response to climatic changes over several time scales.

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Figure legend

Fig. 1 Saharan dust sources from literature [33,35] (A1-4); [36] (M1-3, S1-2). Arrows indicate the main routes and the amount per year of dust outbreaks toward MED and continental Europe (modified after [29]).

Fig.2 Arrows indicate the location of sampling sites for which time series of atmospheric data are available. Division in sub-areas 1-10 according to [114] for budget calculations (modified after [16]).

Fig. 3 – Time series of spatially averaged chlorophyll computed for a window of 4-5 days before and 9-10 days after the event on April 9, 2000 for the EMED (area around Crete: squares) and the event on July 17 for the WMED (area between Sicily, Sardinia and Tunisia: triangles). Zero on the X axis corresponds to the event day. A rise in chlorophyll from 0.2 to 0.6 mg m^{-3} is evident starting in the EMED. The response in the WMED seems be slower: there is a 2-3 days time lag between the dust event and the rise in chlorophyll (from 0.1 to 0.4 mg m^{-3}).

Fig. 4 – Atmospheric impact on the euphotic zone. N,P and Fe figures are average MED fluxes. Mass balance shows that N fluxes, as with Fe fluxes, require a sink in excess of the equivalent P.

Fig. 5 - The effect of excess C strategies on total biomass. In the absence of both carbonate and exudate formation (solid line); with only diatom exudation (dotted line); with only coccolithophorid carbonate production (broken line) in the presence of both carbonate and exudates production (thick solid line).

Fig. 6 - The effect of atmospheric Fe on the model. The model (above) shows maximum biomass at MED iron fluxes (30-60 µmol m^{-2} d^{-1}), and less when Fe fluxes are lower or higher. CO3-C (below, left) and Org-C (below, right) fluxes are inversely proportional.

Tables

Tab. 1 Concentration of insoluble particulates in air and rain in Sardinia, Italy.

	MSP				TPC			
Type of event	AM	GM	R	No	AM	GM	R	No
Background	2.8	2.4	0.5-5	60	1.8	0.7	0.01-4	15
Saharan enriched	6.9	6.8	2-10	30	8.6	8.5	7-12	5
"pure"	15.9	15.0	8-24	8	22.2	8.5	6-55	9
"outbreak"	44	43.9	40-47	2	323	263	135-512	2

MSP = mineral suspended particulate in aerosols ($\mu g\ m^{-3}$); TPC = total particulate content in rain ($mg\ l^{-1}$);
AM = arithmetic mean; GM = geometric mean; R = range; No. = number of samples.
Background: Al/Si <0.3; Ca <12%; associated rain pH <5.60; Ca<200 $\mu eq\ l^{-1}$.
Saharan: crust encriched = AI/Si > 0.3; Ca > 2%; "pure" and "outbreaks" = Al > 1000 ng m-'; AI/Si > 0.4; Ca>4%.

Tab. 2 Mean annual (and range) atmospheric mass fluxes ($g\ m^{-2}$) measured at various coastal sites (refer to Fig.2 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 [4]; 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) [57,58]; (b) [59]; (c) [21,40]; (d) [14,47]; (e) [60]; (f) [61,62]; (g) [63].

Table 3 Atmospheric (A) input of insoluble particles to MED Sea. 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 text for explanation).

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

Tab. 4 Annual dust depositions in several areas in the Med basin and in the European areas

Source	Location	Annual deposition (g m^{-2})
[66]	Aegean Sea	11.2–36.5
[67]	Southern Sardinia	6–13
[68]	Swiss Alps	0.4
[69]	French Alps	0.2
[70]	NE Spain	5.1
[47]	Corsica	12
[14]	Corsica	12.5
[71]	Central France	1
[62]	Crete	10–100
[63]	Israeli coast	72
[63]	SE Mediterranean	36

Table. 5 Particle size distributions of Saharan dust in several area in the MED basin and in the European area

Source	Location	Modal, mean or median size (μm)
[73]	Crete	8–30 modal
[74]	Spain	4–30 mean
[75]	West Germany	2.2–16 median
[62]	Crete	4–16 median
[21]	Sardinia	8-40 modal
[71]	SW France	4–12.7 median
[76]	South of France	8–11 median
[77]	Central Mediterranean	2–8 modal
[78]	Paris Basin France	8 modal
[68]	Swiss Alps	4.5±1.5 median
[79]	Central and Southern Sardinia	12-16 median

Tab. 6 Average of clay mineral compositions and I/K ratio in Saharan dusts in MED basin.

Sample	Illite	Chlorite	Kaolinite	Smectite	I/K
WMED	53	9	29	9	1.8
CMED	66	12	16	3	4.0
EMED	32	5	38	25	0.8

This average was compiled using data from several authors:

[50] 3 samples, [95] 3 samples, [34] 10 samples for the WMED; [95] 3 samples, [96] 3 samples for the CMED; [96] 7 samples, [45] 17 samples; [87] 8 samples for the EMED.

Tab. 7 -Total nitrogen deposition

	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[e]					
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

(a) [115]; (b); (c) [41]; (d) [113]; (e) p = particulate, g = gaseous species.

Tab. 8 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) [126] Migon (1989); (c) [125] Bergametti et al. (1992); (d) [127] Loÿe-Pilot (unpublished results);
(e) [63] Herut and Krom (1996).

Tab. 9 Atmospheric (A) inputs of nitrogen and phosphorus (all in tons *10^3 yr^{-1}). Data on N atmospheric input from [113]; 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 (10^6km^2)**	**Nitrogen A**	**Phosphorus A**
WMED	0.84	459	29
CMED	0.80	346	22
EME	0.70	263	15
Total	**2.34**	**1068**	**66**
%		*51*	*33*

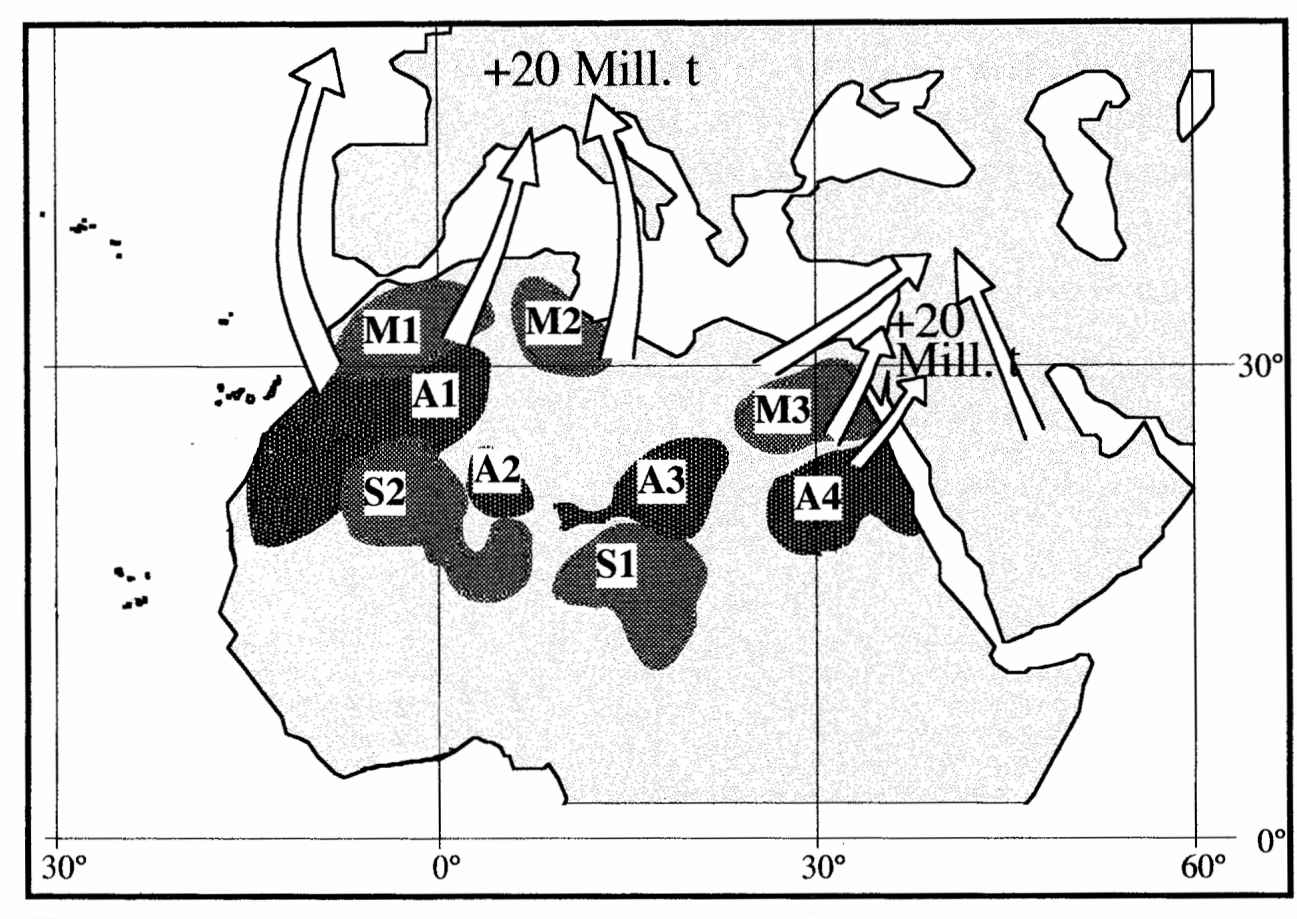
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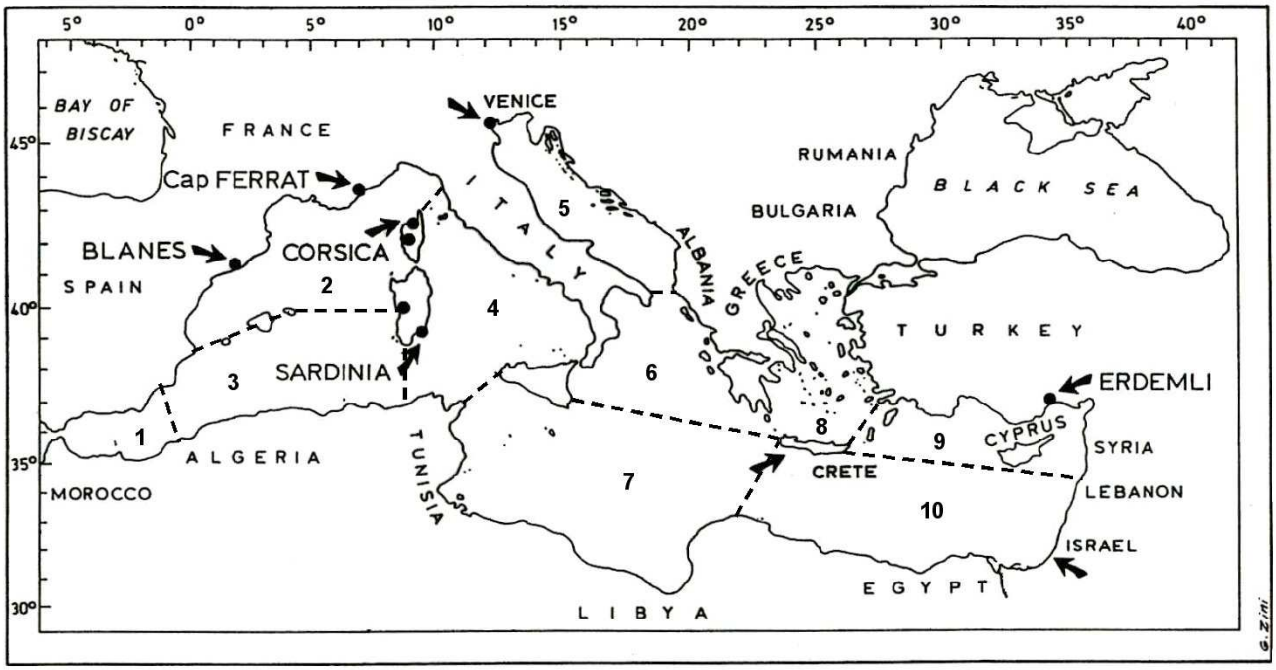
Fig. 1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ALGERIA
MOROCCO
TUNISIA
VENICE
ITALY
ALBANIA
GREECE
RUMANIA
BULGARIA
BLACK SEA
TURKEY
ERDEMLI
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Fig. 2

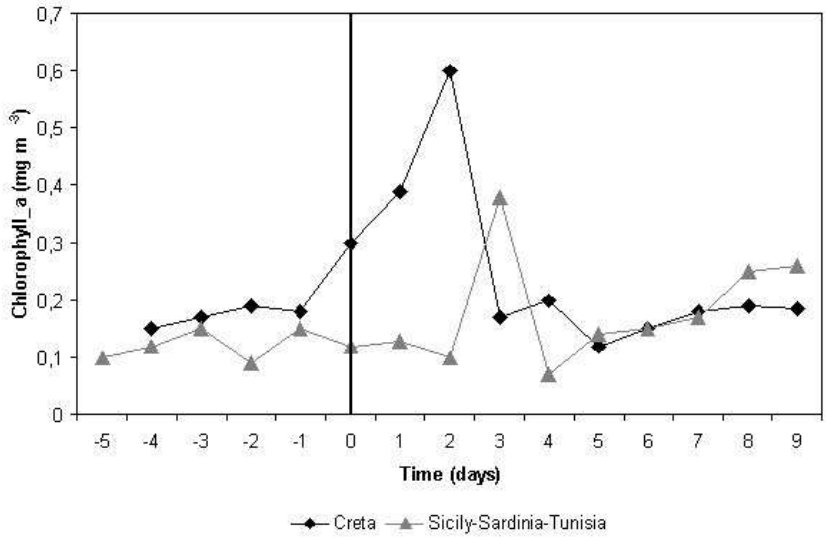


Fig. 3

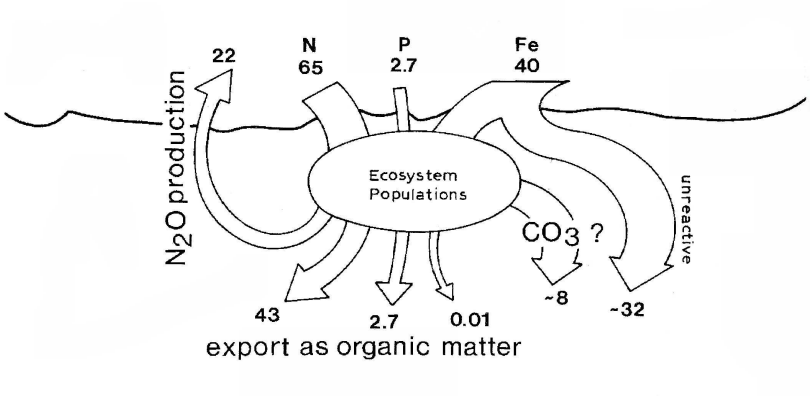
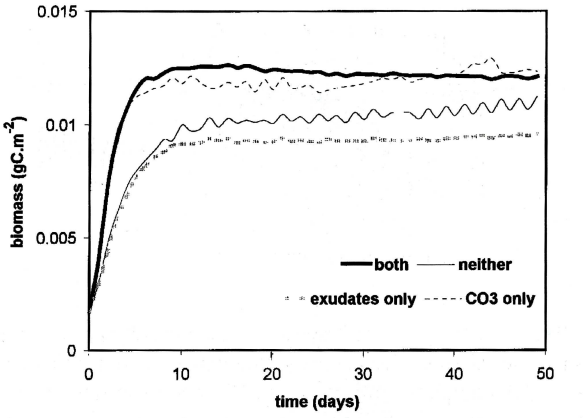


Fig. 4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0
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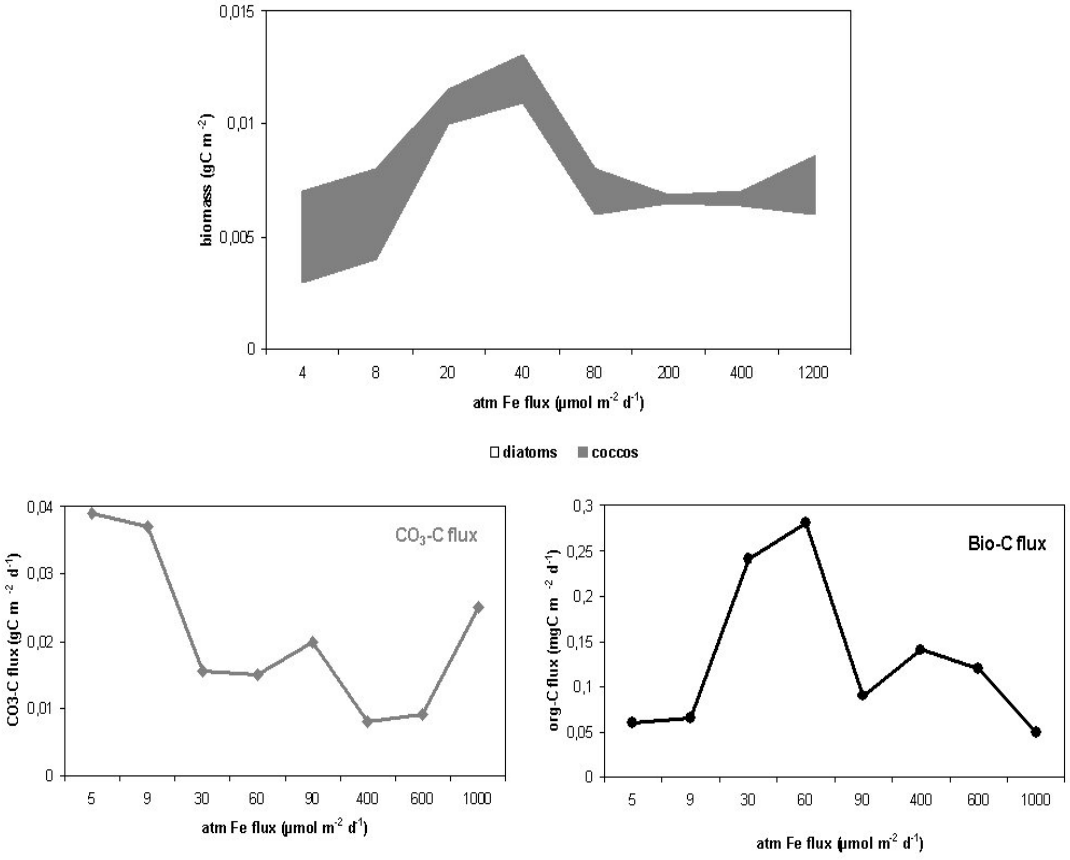
both
neither
exudates only
CO3 only
0
10
20
30
40
50
time (days)

Fig. 5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1200
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diatoms
coccos
0,04
0,03
0,02
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0
CO3-C flux (gC m-2 d-1)
CO3-C flux
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9
30
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90
400
600
1000
atm Fe flux (µmol m-2 d-1)
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0,25
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0,15
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org-C flux (mgC m-2 d-1)
Bio-C flux
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400
600
1000
atm Fe flux (µmol m-2 d-1)

Fig. 6