

## Saharan input of phosphate to the oligotrophic water of the open western Mediterranean Sea

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### Abstract

A Saharan soil, considered as a proxy for Saharan aerosols, was used to perform a series of dissolution experiments: various amounts of Saharan soil were exposed to ultrapure water and seawater for varying lengths of time. The concentration of phosphate released was proportional to the amount of dust introduced. In the case of Saharan events associated with a significant amount of rain, the main dissolution of phosphorus will occur in the air column; for Saharan events associated with only few drops of rainwater, the main dissolution will occur in the surface seawater. Saharan dust represents a source of phosphate to the surface water and may play a role in biological activity, especially during the oligotrophic period. In the western Mediterranean in oligotrophic conditions, biological production is P-limited, and the atmosphere becomes the main pathway of nutrients to the surface mixed layer. At the scale of the oligotrophic season, the input of "Saharan dissolved inorganic phosphorus (DIP)" are negligible compared with the new production integrated over the productive layer. At the event timescale, the production induced by "Saharan DIP" can represent up to 15% of the integrated new production and up to 14% of the total primary production in the mixed surface layer. These inputs of atmospheric DIP would promote fixation of atmospheric N<sub>2</sub> that, in return, may enhance the new production in the surface layer.

The atmosphere is a major pathway for the transport of many natural and anthropogenic materials from continents to the oceans (Duce et al. 1991; Jickells 1995). Over the past 20 years, it has been clearly shown that the atmosphere can be an important route by which nutrients, such as phosphorus, nitrogen, and iron, are delivered to surface waters (Graham and Duce 1982; Duce 1986; Prospero et al. 1996; Paerl et al. 1999). The effect of such atmospheric inputs of nutrients on biological cycles could be particularly important in the case of oligotrophic oceanic areas and semienclosed seas such as the Mediterranean Sea (Loÿe-Pilot et al. 1990; Bergametti et al. 1992; Guerzoni et al. 1999; Herut et al. 1999a; Migon and Sandroni 1999; Sarthou and Jeandel 2001; Guieu et al. in press).

The western Mediterranean Sea receives atmospheric phosphorus from two main sources: a crustal source, from the North African desert belt in the south (Bücher 1989; Avila et al. 1998; Herut et al. 1999b) and an anthropogenic source from the north, from the industrialized European countries (Bergametti et al. 1992). The phosphorus associ-

ated with the marine source is negligible (Bergametti et al. 1992). When aerosols come in contact with raindrops, a part of the particulate inorganic phosphorus associated with the particles can dissolve into orthophosphate form (PO<sub>4</sub><sup>3-</sup>) (denoted as dissolved inorganic phosphorus [DIP]) that may be assimilated by the biological community.

This study focuses on the Saharan source of phosphate, because the western Mediterranean Sea receives considerable amounts of mineral particles. Loÿe-Pilot and Martin (1996) estimated the mean annual input of Saharan dust to the western Mediterranean at 12 tons km<sup>-2</sup> yr<sup>-1</sup> for the period 1984–1994. This flux represents ~90% of the total atmospheric particulate fallout to the water column (Loÿe-Pilot and Martin 1996). At present, Saharan dust deposition in the western Mediterranean Sea is ~4 tons km<sup>-2</sup> yr<sup>-1</sup> (Ridame et al. 1999). Wet deposition is considered to be a highly effective mechanism of dust deposition in the whole western Mediterranean Sea (Prodi and Fea 1979; Guerzoni et al. 1997; Loÿe-Pilot and Martin 1996) and is characterized by short-lived events of high magnitude. Loÿe-Pilot and Martin (1996) demonstrated that the dry deposition of Saharan dust is a negligible pathway relative to wet deposition in this area. Very significant amounts of Saharan dust are deposited with only a few drops of rainwater. These events have been reported by some authors as dry events, because rain drops evaporate immediately. We took into consideration that these particular inputs are associated with the wet deposition. By comparison, in the eastern Mediterranean, the dry deposition of Saharan dust can represent up to 56% of the annual total deposition (Kubilay et al. 2000).

Because Saharan aerosols contain particulate phosphorus, these sporadic events may play an important role in the phosphorus cycle in the Mediterranean and the marine ecosystem may benefit from inputs of "Saharan DIP," especially during oligotrophic situations that occur during the period of stratified waters. DIP is an essential nutrient for the

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growth of marine biological communities and is often the nutrient controlling oceanic biological production. In the western Mediterranean, during the oligotrophic period (generally from June to October), the surface waters are isolated from intermediate and deep waters. Consequently, the surface mixed layer is nutrient depleted. In the western Mediterranean Sea, DIP appears to be the principal limiting nutrient for the phytoplanktonic and bacterial production during this period (Thingstad and Razzoulzadegan 1995; Vulot et al. 1996; Thingstad et al. 1998). One explanation for the P limitation, proposed by Krom et al. (1991), is that Saharan dust may remove DIP from the water column through adsorption processes. During this period, the atmosphere becomes the primary pathway for DIP input to the surface waters, and, during this same period, the frequency and the magnitude of Saharan pulses are greatest over the western Mediterranean (Bergametti et al. 1989; Lojé-Pilot and Martin 1996). Studies have shown that the input of atmospheric nutrients by a rain shower may trigger phytoplankton growth during oligotrophic conditions (Martin et al. 1989; Klein et al. 1997). Dulac et al. (1996) showed that by coupling Meteosat data, used to observe African dust transport, with coastal zone color scanner (CZCS) data, used to monitor marine biology activity in the western Mediterranean, a correlation seems to be present between strong desert dust events and an increase of chlorophyll concentration. During the winter, vertical mixing is intense and provides DIP to the surface layer. Under these conditions, the input of atmospheric DIP may be unimportant.

The objectives of this article are to (1) quantify the dissolution processes affecting phosphorus associated with the Saharan aerosols, (2) estimate the DIP flux originating from the Saharan source, and (3) evaluate, in terms of new production, the potential effect of these inputs of "Saharan DIP" to the surface waters under oligotrophic conditions. This article will focus exclusively on phosphate, because the other nutrients associated with Saharan dust, such as iron, are out of the scope of the study. In fact, Saharan dust governs the cycle of iron, because these particles represent the main source of dissolved iron for the western Mediterranean waters (Guieu et al. in press). It has, however, been recently hypothesized that iron may play a significant role in biological ecosystems in the western Mediterranean Sea (e.g., Sarthou and Jeandel 2001). The input of nitrogen compounds originating from the Saharan source are negligible (Lojé-Pilot et al. 1990; Guerzoni et al. 1999).

### Characterization of Saharan soil

Saharan soil, representative of the Saharan aerosol carried over the western Mediterranean Sea, was used for all the *in vitro* experiments. This choice was motivated by several factors. (1) Saharan aerosols collected far from the source region are generally mixed with anthropogenic particles (Guieu et al. 1997). Thus, by use of a Saharan end member, the dissolution processes associated specifically with the Saharan source can be characterized. (2) During their transport, Saharan aerosols in contact with raindrops undergo dissolution processes (Guieu and Thomas 1996; Desboeufs et al.

1999) that affect their chemical properties and, consequently, their concentrations. Moreover, the use of soils is experimentally convenient, because the amount of particles is large enough to avoid any limitations in the particle weight necessary for all the experiments.

Surface soil samples were collected under clean conditions, in southern Algeria, a region considered to be a significant source of Saharan dust for the western Mediterranean Sea (Bergametti et al. 1989; Molinaroli et al. 1993). Sampling sites were chosen on the basis of their isolation from any contamination sources (see details and location in Guieu and Thomas 1996). All samples were regrouped, to obtain a composite Saharan soil.

*Grain size distribution*—After a long-range transport across the Mediterranean (1000–2000 km away from the source), the size distribution of Saharan dust shifts to particles <20  $\mu\text{m}$  in diameter (Schütz and Sebert 1987; Molinaroli et al. 1993; Guieu et al. in press). To be representative of the grain-size distribution of Saharan aerosols, the soil samples were hand sieved in a laminar flow bench, through successive clean polyethylene meshes of 100- and 20- $\mu\text{m}$  pore diameter (see arguments and discussion in Guieu et al. in press). The smallest fraction (<20  $\mu\text{m}$ ) was stored in an acid-washed glass bottle and was used for all of the experiments described in this article.

*Mineralogical and carbon analysis*—The composite soil was analyzed by use of an X-ray diffraction technique to determine its mineralogical composition (semiquantitative analysis). In the nonclay fraction, quartz was the dominant constituent (~20%). The other main constituents were feldspar (~10%–15%), calcite (<5%), dolomite, hematite, and amphibole (~1%). The clay fraction represented ~50% of the total mineralogical composition. The clay fraction was dominated by the smectite (~42%), kaolinite (29%), illite (~17%), palygorskite (~5%), and chlorite (~7%). Indeed, the mineralogical composition of the soil sample was characteristic and representative of the average mineralogical composition of a Saharan aerosol (Bücher et al. 1983; Schütz and Sebert 1987; Molinaroli et al. 1993; Guerzoni et al. 1997; Avila et al. 1998). No apatite was identified by X-ray diffraction (<1%) because the present concentration was below the detection limit of the analyzer (~1%). When an analytical method of highest sensitivity, the scanning electron microscope with energy dispersion system was used, some apatite was detected at trace level. Likewise, Coudé-Gaussen (1982) have detected some grains of apatite in Saharan soils and aerosols.

Total (inorganic and organic) and organic carbon concentration analyses were performed on eight aliquots by use of a carbon, hydrogen, nitrogen analyzer (LECO 900). To determine the organic carbon, the inorganic carbon associated with the carbonates was first dissolved with HCl (2N) in an oven (at 70°C). The total and organic carbon levels of the composite soil were, on average, 0.80%  $\pm$  0.05% and 0.43%  $\pm$  0.02%, respectively (by weight). The inorganic carbon was 0.36%  $\pm$  0.05%. The concentration of organic carbon in the composite soil was of the same order found by Lepple and Brine (1976), who found organic carbon in Saharan soils

Table 1. Concentrations of total phosphorus (in % of the total mass) in various Saharan soils.

Reference	Type of sample	% of total P
This study (<20 $\mu\text{m}$ )	Composite soil, south of Algeria	$0.14 \pm 0.01$
Guieu et al. (in press) (<20 $\mu\text{m}$ )	13 soils collected over north Africa, (including the soil used in the present study)	$0.07 \pm 0.03$
Herut et al. (1999b) (<63 $\mu\text{m}$ )	Loess of Negev desert, Israel	0.04
Graham and Duce (1979) (<30 $\mu\text{m}$ )	Libyan desert	0.07
Lepple (in Graham and Duce 1979)	Northwest coast of Africa	0.13
Mean and SD		$0.08 \pm 0.03$

to be  $0.7 \pm 0.5\%$ . Because the amount of organic matter is approximately twice that of organic carbon, the percentage of organic matter in the composite soil is  $\sim 1\%$ , consistent with the average content of organic matter in the Saharan aerosol: 1%–3% (Tomadin et al. 1984).

**Phosphorus analysis**—Eight aliquots of the soil sample were acid-digested inside a microwave oven (Milestone 1200 Mega) with 4 ml of  $\text{HNO}_3$  (Suprapur) (see details in Ridame et al. 1999). Ten aliquots of MESS-2 reference material (National Council of Canada) and five reagent blanks were digested following the same protocol. Total phosphorus concentrations were determined by use of the colorimetric method of Murphy and Riley (1962) by manual spectrophotometry (Anthelie Data). Results obtained on the certified reference material indicated a mean recovery of  $100\% \pm 7\%$ . The low coefficient of variation showed a high reproducibility of results. The detection limit, defined as three times the standard deviation of the blank, was  $0.02 \mu\text{M}$ . Triplicate measurements of DIP were taken, and the reproducibility was  $\sim 5\%$ .

The total phosphorus in eight aliquots of soil was, on average,  $0.14\% \pm 0.01\%$  (by weight). This concentration is of the same order of magnitude as those found in a large spectrum of Saharan soils analyzed by different authors (Table 1). The minimum and maximum concentrations of phosphorus in Saharan end member were 0.04% and 0.14%, respectively (mean,  $0.08\% \pm 0.03\%$ ). The coefficient of variation was relatively high ( $\sim 45\%$ ), probably because of different grain size distributions of soils and a spatial variation of phosphorus in the sampled regions. It should be noted that most of phosphorus in Saharan soils seemed to be present in inorganic form ( $\sim 90\%$ ) (Herut et al. 1999b); a fraction

of phosphorus could also be found in organic form. In this study, we focused exclusively on inorganic phosphorus because phosphate (DIP) is the preferred form available for living organisms. The phosphorus concentration in the Saharan aerosol over the western Mediterranean has been found to be relatively homogeneous, ranging from 0.06% to 0.20% (mean,  $0.09\% \pm 0.04\%$ ) (Table 2). Thus, the mean phosphorus concentration of Saharan end-member soils and aerosols were of the same order of magnitude.

#### Methodology for the in vitro dissolution experiments

The composite Saharan soil was carefully homogenized prior to each experiment. In vitro experiments were performed in a clean laboratory.

**In ultrapure water**—Various amounts of the sample were introduced into acid-washed glass bottles filled with filtered ultrapure water (produced by a Milli-Q system, pH  $\sim 5.5$ ). The final particulate concentrations ( $P_c$ ), ranging from 5 to  $8000 \text{ mg L}^{-1}$ , were representative of the natural particulate concentrations observed for Saharan rains (Loÿe-Pilot pers. comm.), where 60% of 691 rains, over a 13-yr period, had particulate concentrations between 5 and  $8000 \text{ mg L}^{-1}$ . Thirty percent of the events ( $n = 206$ ) had particle concentrations between 0.1 and  $5 \text{ mg L}^{-1}$ . Because of problems in quantifying weight, it was not possible to represent this class of dust concentrations. The rains having particle concentrations  $>8000 \text{ mg L}^{-1}$  represented 10% ( $n = 55$ ) of the total number. For the low concentrations of Saharan dust ( $5\text{--}40 \text{ mg L}^{-1}$ ), experiments were conducted in triplicate. For concentrations ranging from 50 to  $200 \text{ mg L}^{-1}$ , experiments were conducted in duplicate. The difference between data

Table 2. Concentration of total phosphorus (in % of the total mass) in Saharan aerosols (particulate phase of Saharan rains and aerosols collected by pumping). The concentrations found in the particulate phase of rains were not corrected from the dissolution of carbonates (except for the values proposed by Guieu et al. in press).

Reference	Type of sample	$n$	% of total P
Bücher (1989)	Particulate phase of Saharan rains	2	0.06 and 0.13
Avila et al. (1998)	Particulate phase of Saharan rains	5	$0.06 \pm 0.03$
Guieu et al. (in press)	Particulate phase of Saharan rains	10	$0.08 \pm 0.01$
Tomadin et al. (1984)	Pumping of aerosols in Adriatic Sea and at Bologna and Messine	5 and 2	$0.08 \pm 0.02$ and $0.18 \pm 0.03$
Lepple (in Graham and Duce 1979)	Pumping on the northwest coast of Africa	—	0.20
Lepple (in Graham and Duce 1979)	Pumping of aerosol in Mauritania	—	0.11
Mean and SD			$0.09 \pm 0.04$

obtained between replicates was <10%. Three exposure durations were chosen to simulate natural conditions: 10 min and 12 and 24 h. These durations of exposure are representative of the contact time between the dust and the raindrops during transport over the Mediterranean Sea (Bergametti et al. 1989). During incubation, the bottles were gently stirred. The samples were then filtered through 0.4- $\mu\text{m}$  Nuclepore membrane (polycarbonate, diameter of 47 mm), and the pH was measured on selected aliquots. The dissolved phase, collected in an acid-washed glass bottle, was acidified to pH  $\approx 2$  (with Suprapur-Merck HCl). Five blanks, treated as samples (without dust), were also performed to estimate the amount of contamination introduced during the experiment (filtration, acid used, and glass bottle), and the adsorption effect into the walls of the bottle was checked. The DIP measurements in both cases were below the detection limit of the spectrophotometer (0.02  $\mu\text{M}$ ). For the low dust concentrations, filtrates (100–1000 ml) had to be concentrated by evaporation in order for the concentrations to be detected by spectrophotometer. The evaporation was performed inside a 1-liter Teflon beaker on a hot plate (at  $\approx 90^\circ\text{C}$ ) under laminar air flow. When the volume reached  $\sim 50$  ml, the concentrated sample was then analyzed by use of spectrophotometry (concentration factor between 2 and 20). Standard phosphate solutions (Merck Suprapur), ranging from 0.01 to 0.05  $\mu\text{M}$ , were used to evaluate the reliability of the evaporation process (concentration factor similar to that of the samples). The mean recovery was satisfactory and reproducible (101%  $\pm$  7%;  $n = 11$ ). Five evaporation blanks (concentration factor similar to that of the samples) that used ultrapure water were also performed, to estimate an eventual contamination during the evaporation phase; the resulting values, including all processing steps (concentration step, eventual contamination by reagents used, glass bottle, and filtration) were below the detection limit.

*In seawater*—The protocol used was similar to the one described above. The seawater was sampled at 50 m depth, in June (oligotrophic period), at the DYFAMED site (see details in the Discussion section) and was filtered through a 0.2- $\mu\text{m}$  Nuclepore membrane (polycarbonate). The initial concentration of DIP in this filtered seawater was undetectable (<0.02  $\mu\text{M}$ ). Various amounts of Saharan dust, from 5 to 100 mg, were introduced in 1-liter glass bottles filled with seawater poisoned with  $\text{HgCl}_2$  (final concentration in the sample, 24 mg  $\text{L}^{-1}$  of  $\text{HgCl}_2$ ). During incubation, the bottles were gently stirred. At the end of each contact time, two aliquots were sampled and filtered through a 0.4- $\mu\text{m}$  Nuclepore membrane (polycarbonate); the dissolved phase, collected in an acid-washed glass bottle, was acidified to pH  $\approx 2$  (with Suprapur-Merck HCl). The reproducibility of DIP measurements between the duplicated aliquots was <5%. Blanks, treated as samples, were also performed to estimate the amount of contamination introduced by the  $\text{HgCl}_2$  solution, filtration, acid use, and glass bottle. The adsorption effect into the walls of the bottle was checked. In both cases, the DIP measurements were below the detection limit of the spectrophotometer. The exposure time chosen to simulate the natural conditions were 6, 24, and 48 h and 1 week. They were longer than those chosen for the ultrapure water dis-

solution because particles will stay for a long time in seawater.

### Collection of the rainwater (wet deposition)

Between January 1999 and January 2000, wet deposition was collected at Villefranche-sur-mer, on the southeastern coast of France (43°41'N, 7°19'E). The collection was performed on a per-event basis by use of a bulk plastic collector (Météo France Standard rain gauge). The collector had a 398  $\text{cm}^2$  surface collection area and was situated 1 m above the ground. A polyester mesh (pore size 33  $\mu\text{m}$ ) covered the collector to prevent insects and organic debris from falling inside. At the end of each rain, the water was collected and filtered through preweighed Nuclepore membranes (pore size 0.4  $\mu\text{m}$  and diameter 47 mm). The filters were then dried inside an oven for 24 h (at  $50^\circ\text{C}$ ). The pH and amount of rainfall were determined for each rain. The weight of particulate material was obtained by calculating the difference between the weight of the dried filter before and after filtration. For the case of mixed events, the weight of the polluted component (defined as black particulate matter originating from anthropogenic activities and composed by very small particles) was generally <2 mg per filter (Loÿe-Pilot et al. 1986; Loÿe-Pilot and Martin 1996) and was estimated and subtracted from the total weight, to obtain the contribution of the Saharan material. The aim of this field work was to sample the Saharan events and to measure the associated particle flux. No chemical analysis was performed because the site was not remote and local sources of anthropogenic phosphorus (from an incineration plant) were suspected by Migon et al. (2001). It was noted that, during this sampling year, no dry deposition was evident, and that all the deposition came with rain events. Rainfall during some of these events was not measurable, which is in strong agreement with the fact that the dry deposition is negligible in western Mediterranean (Loÿe-Pilot and Martin 1996). Three-dimensional, 4-d backward air-mass trajectories at 850 and 700 hPa barometric level have been established by the French National Meteorology for each Saharan rainfall collected during the sampling period ( $n = 26$ ). This calculation is based on the model established by Martin et al. (1987), which has been validated concerning the transport of Saharan dust by Martin et al. (1990). These trajectories allowed the identification of the major sources of atmospheric phosphorus for each event: soil-derived dust from desert areas of North Africa and/or anthropogenic emissions from European countries.

### Results

*Dissolution in ultrapure water*—Figure 1 presents the relationship between the mean DIP released by the dust as a function of the Saharan dust amount introduced in ultrapure water for three durations of exposure (10 min and 12 and 24 h). The relationships follow typical power laws with a high correlation coefficient ( $0.96 < r^2 < 0.99$ ). The DIP released was proportional to the amount of dust introduced; it was greatest for the particle concentrations representative

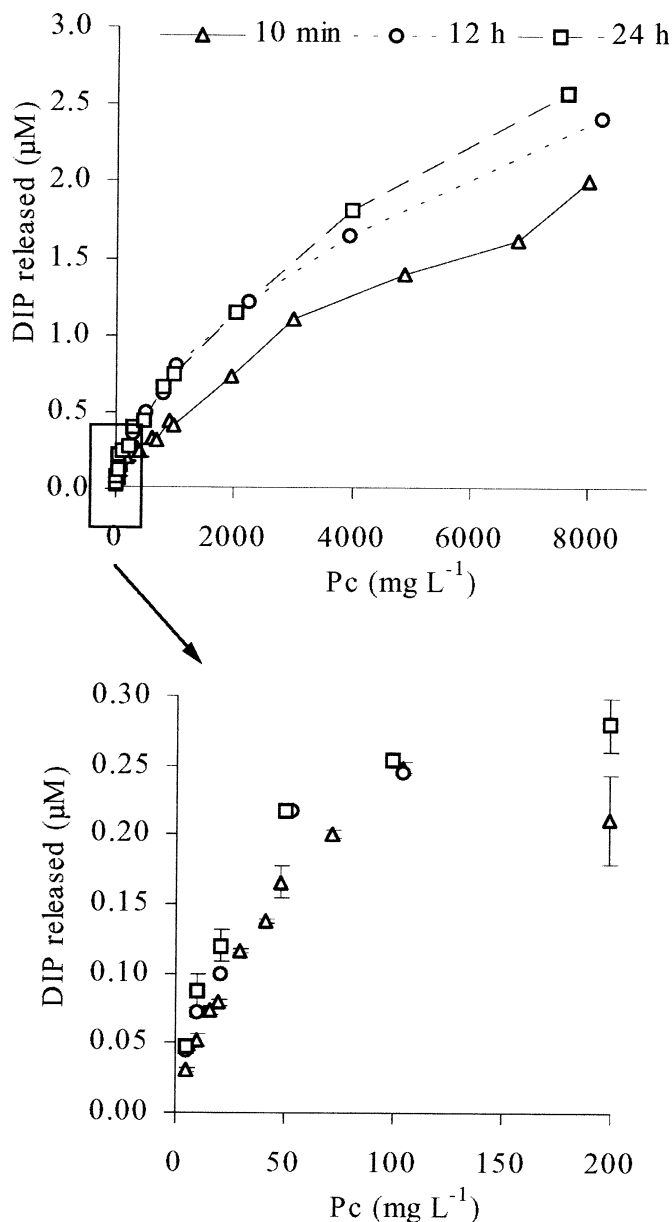


Fig. 1. Dissolution in ultrapure water: mean DIP released by the dust ( $\mu\text{M}$ ) as a function of the amount of Saharan dust introduced in ultrapure water ( $P_c$ ,  $\text{mg L}^{-1}$ ), for three durations of exposure (10 min and 12 and 24 h).

of a high-intensity Saharan event ( $8000 \text{ mg L}^{-1}$ ), reaching up to  $2.0 \mu\text{mol L}^{-1}$  ( $\mu\text{M}$ ) (contact time 10 min) to  $2.6 \mu\text{M}$  (contact time 24 h). The lowest value of DIP was found in experiments where particle concentrations were representative of low-intensity Saharan events ( $P_c = 5 \text{ mg L}^{-1}$ ) and ranged from  $0.03 \mu\text{M}$  (contact time 10 min) to  $0.05 \mu\text{M}$  (contact time 24h) (Fig. 1, inset). In all cases, the concentration of DIP increased with increasing contact time of particles in water (Fig. 2). As seen in Fig. 2, the rate of phosphorus dissolution was relatively rapid. After a contact time of 10 min, the greater part of the dissolvable phosphorus was released.

From these in vitro experiments, the percentage of dis-

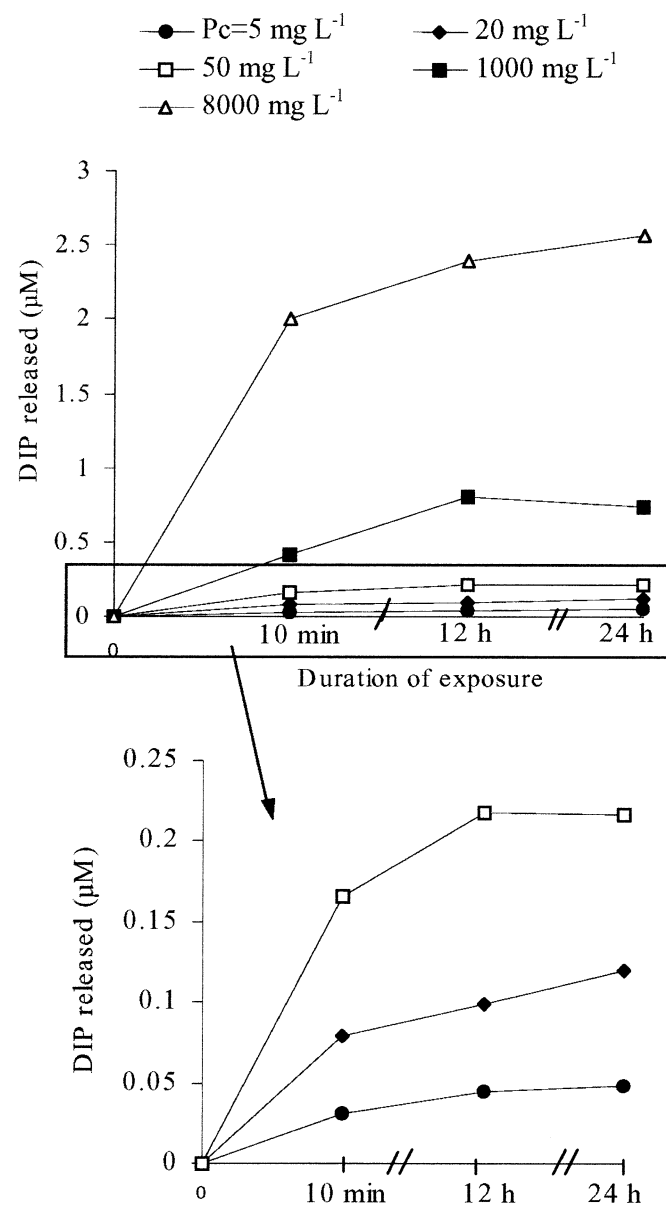


Fig. 2. Dissolution in ultrapure water: mean DIP released by the dust ( $\mu\text{M}$ ) as a function of the duration of exposure: 10 min and 12 and 24 h, for various Saharan dust amounts ( $P_c$ ,  $\text{mg L}^{-1}$ ), introduced in ultrapure water.

solved phosphorus,  $D_{rw}$ , in ultrapure water, can be calculated. It is defined as follows:

$$D_{rw}(\%) = \frac{\text{DIP}_{\mu\text{M}} \times 100}{P_{\text{total}_{\mu\text{M}}}}$$

where  $D_{rw}$  is the percentage of DIP,  $P_{\text{total}}$  ( $\mu\text{M}$ ) is the concentration of total phosphorus in the sample  $[(P_c \times 0.14 \times 1000)/(30.97 \times 100)]$ , atomic weight is  $30.97 \text{ g mol}^{-1}$ ,  $P_c$  is the amount of Saharan particles introduced (in  $\text{mg L}^{-1}$ ), and 0.14 is the percentage of total phosphorus in the composite soil.

The relationship between the percentage of dissolved phosphorus and the amount of dust in ultrapure water for

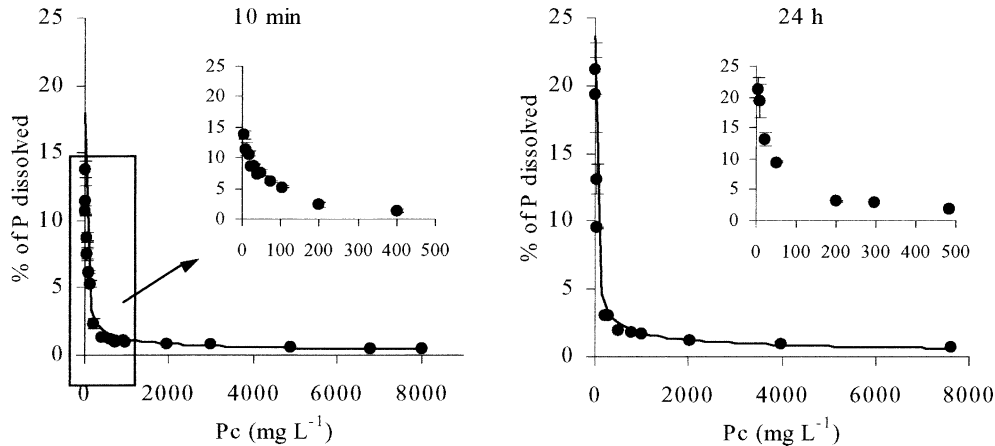


Fig. 3. Dissolution in ultrapure water: percentage of dissolved inorganic phosphorus ( $D_{rw}$ ) released by dust as a function of the amount of Saharan dust introduced in ultrapure water ( $P_c$ ,  $\text{mg L}^{-1}$ ) for contact times of 10 min and 24 h.

the three contact times is shown in Fig. 3. The correlation coefficient,  $r^2$ , ranged from 0.96 to 0.99. For the three contact times, the percentage of dissolved phosphorus was inversely proportional to the amount of dust introduced. For concentrations ranging from 5 to 200  $\text{mg L}^{-1}$ , the percentage of DIP decreased rapidly, by a factor of 6–7 (see Fig. 3, inset). The highest mean values were witnessed for small dust concentrations (5  $\text{mg L}^{-1}$ ): 14%, 19%, and 21%, respectively, for contact times of 10 min and 12 and 24 h. The percentage of DIP was lowest for the  $P_c$  concentration representative of events of high intensity ( $>500 \text{ mg L}^{-1}$ ) and remained roughly constant,  $\sim 0.5\%–2\%$  for the three contact times.

For the  $P_c$  ranging from 5 to 50  $\text{mg L}^{-1}$ , the final pH varied from 5.5 to 6, which is lower than the pH observed

for a typical Saharan rain ( $\text{pH} > 6$ ). For the highest particle concentrations, the partial dissolution of carbonates increases the pH to 8, a typical pH of that measured in Saharan rains (Guieu and Thomas 1996). Consequently, if the dissolution of Saharan phosphorus increases when the pH decreases, the dissolution of phosphorus, in our experiment, may have been enhanced for the low dust concentrations. On the other hand, within the range of particle concentrations 0–50  $\text{mg L}^{-1}$ , which is representative of Saharan events of low intensity (this class of  $P_c$  represents 60% of the field data), the particles generally are associated with anthropogenic particles, and these “mixed” events are characterized by a pH varying from 4 to 6 (Loÿe-Pilot and Morelli 1988). From the 13-yr series of Saharan rains, 80% of Saharan rains with a  $P_c < 50 \text{ mg L}^{-1}$  had a pH value ranging between 4 and 6 and 60% had a pH value  $< 5.5$  (Loÿe-Pilot pers. comm.). Consequently,  $\sim 35\%$  of the total number of Saharan rains recorded in Corsica during 13 yr had a pH value  $< 5.5$ , which is lower than the final pH in our dissolution experiments. Thus, the dissolution of Saharan phosphorus, for low  $P_c$ , could be underestimated in the experiments if the dissolution process at pH values between 4 and 5.5 presents a significant variation.

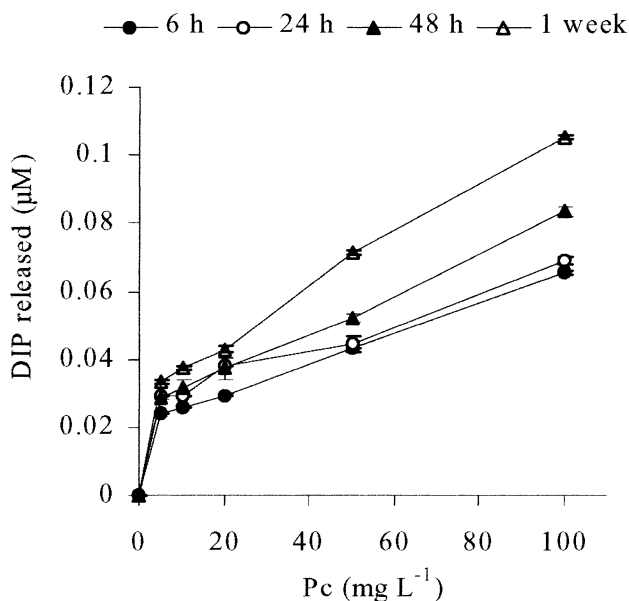


Fig. 4. Dissolution in seawater: mean DIP released by the dust ( $\mu\text{M}$ ) as a function of the amount of Saharan dust introduced in DIP-free seawater ( $P_c$ ,  $\text{mg L}^{-1}$ ), for various durations of exposure.

*Dissolution in seawater*—The aim of these experiments was to determine whether any additional phosphorus dissolution, beyond that which takes place in rainwater, occurs in seawater. The dust concentrations chosen ( $P_c$ ) were not representative of those measured in the surface layer. For analytical reasons, the concentration of DIP released by  $P_c < 5 \text{ mg L}^{-1}$  was undetectable. The lowest  $P_c$  used (5  $\text{mg L}^{-1}$ ) can be considered the highest value measured in the first meter of seawater after a Saharan event of high magnitude. The DIP concentration released was proportional to the amount of dust introduced (Fig. 4). The maximum concentration of DIP released was observed for the highest particle concentrations (100  $\text{mg L}^{-1}$ ), varying from 0.07  $\mu\text{M}$  (contact time 6 h) to 0.11  $\mu\text{M}$  after 1 week. The minimum value of DIP released, corresponding to the lowest  $P_c$  (5  $\text{mg L}^{-1}$ ), increased to 0.03  $\mu\text{M}$  after 1 week. The concentration of DIP increased with an increase of contact time with particles

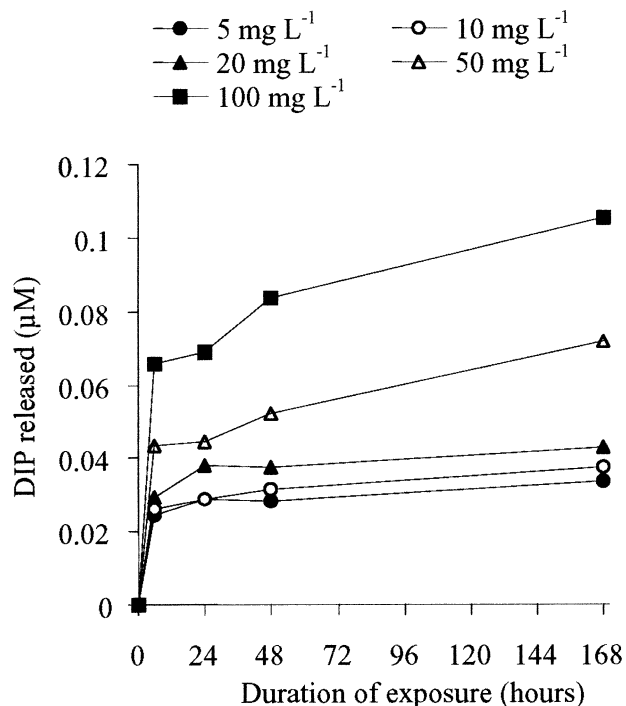


Fig. 5. Dissolution in seawater: mean DIP released by the dust ( $\mu\text{M}$ ) as a function of the duration of exposure (h), for various Saharan dust amounts ( $P_c$ ,  $\text{mg L}^{-1}$ ), introduced in seawater.

in seawater (Fig. 5). After a contact time of 6 h, the concentration of DIP released represented, on average,  $\sim 65\%$  of that released after 1 week. The percentage of dissolved phosphorus in seawater ( $D_{\text{sw}}$ ) was calculated in a similar way to  $D_{\text{rw}}$  in ultrapure water. The values as a function of  $P_c$  are presented for the minimum (6 h) and maximum (1 week) contact time in Fig. 6. The results show that the percentage of dissolved phosphorus varies from 10% (contact time 6 h) to 14% (contact time 1 week) for the lowest  $P_c$  ( $5 \text{ mg L}^{-1}$ ). For the highest  $P_c$  ( $100 \text{ mg L}^{-1}$ ),  $D_{\text{sw}}$  reached a minimum value from 1.4% (6 h) to 2.3% (1 week).

## Discussion

**Factors controlling the dissolution**—In Table 3, the mean percentages of dissolved phosphorus (contact time 24 h) are presented for low ( $5\text{--}20 \text{ mg L}^{-1}$ ), average ( $50\text{--}300 \text{ mg L}^{-1}$ ) and high ( $500\text{--}8000 \text{ mg L}^{-1}$ ) particle concentrations. The first class of particle concentrations represents  $\sim 25\%$  of the Saharan events observed in the field (Loÿe-Pilot pers. comm.), and the maximum percentage of DIP is observed for this particle concentration range. The second and third

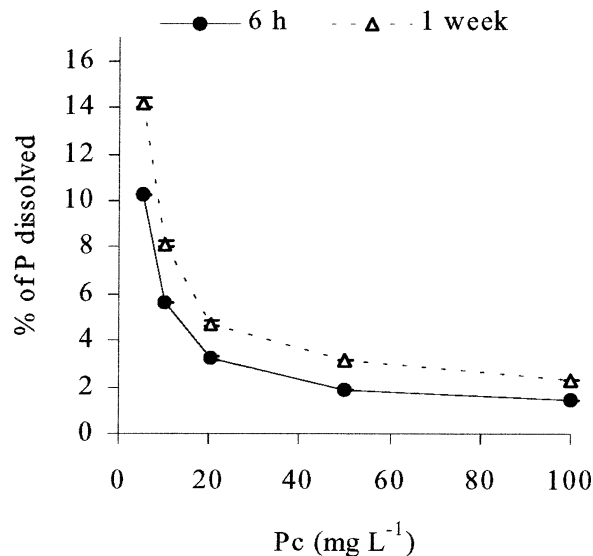


Fig. 6. Dissolution in seawater: percentage of dissolved inorganic phosphorus ( $D_{\text{sw}}$ ) released by dust as a function of Saharan dust amounts ( $P_c$ ,  $\text{mg L}^{-1}$ ), introduced in seawater for the minimum (6 h) and maximum (1 week) contact times.

group each represents 10% of the field data. For the concentration range from  $0.1$  to  $5 \text{ mg L}^{-1}$ , we assumed that the dissolution percentages were of the same order of magnitude, or higher, as those found for  $5 \text{ mg L}^{-1}$ . The particle concentrations ranging from  $0.1$  to  $20 \text{ mg L}^{-1}$  correspond to 55% of the field data, represent the concentrations of Saharan dust most often observed in the field, and have the maximum percentage of phosphorus dissolution (10%–20%).

The dissolution of an element depends on many factors, such as the nature of the particles (Guieu et al. 1997), the grain size of the aerosols, and the pH (Colin et al. 1990).  $P_c$  is also an important factor that is related to the nature of particles (anthropogenic or crustal). In the case of metal dissolution, Guieu et al. (1997) found that the dissolution was greatest for “polluted rains,” where the pH and the particle concentrations were low and the exchange fraction was maximum. In contrast, the dissolution was lowest for Saharan rains where the pH and the particle concentrations were high and the exchange fraction was least. Thus, it appears to be very important to specify the  $P_c$  considered when noting the percentage of dissolution. The partitioning of atmospheric phosphorus between soluble and insoluble forms, in rainwater and seawater, is poorly documented in the literature. In particular, there are few data available on the dissolution of phosphorus associated with a specific source. Losno

Table 3. Mean percentage of dissolved phosphorus ( $D_{\text{rw}}$ ) in ultrapure water (contact time 24 h), for low- to high-intensity Saharan events ( $P_c$  in  $\text{mg L}^{-1}$ ).

Concentration of Saharan particles in rain ( $P_c$ )	$5\text{--}20 \text{ mg L}^{-1}$	$50\text{--}300 \text{ mg L}^{-1}$	$500\text{--}8000 \text{ mg L}^{-1}$
Range of dissolution (in %)	21–13	10–3	2–0.5

(1989) measured the DIP and the particulate phosphorus after filtration of some Saharan rains (pH 6–7) and found that 21%–53% of the total phosphorus was dissolved. From the total aluminum concentration measured in these rains, we calculated the amount of Saharan aerosols ( $P_c$ ) for each rain by considering that the Saharan aerosols contain, on average, 7.1% of Al (Guieu et al. in press). The percentages calculated by Losno (1989) were higher than those found in the present in vitro experiments, and there was no correlation between  $P_c$  and the percentage of dissolution. These differences may be explained by the presence, in collected rains, of anthropogenic phosphorus, which is more labile than the phosphorus associated with Saharan particles. Unfortunately, it is not possible to estimate, from field data, the dissolution of phosphorus associated with a specific source, the rains being generally mixed. The atmospheric phosphorus associated with the Saharan particles seems to be less soluble than the phosphorus associated with anthropogenic aerosols in rainwater and seawater (Graham and Duce 1982; Bergametti et al. 1992; Herut et al. 1999a).

From dissolution experiments of Saharan aerosols in seawater depleted in DIP, Lepple (1975) measured an average dissolution percentage of Saharan phosphorus of 8% (Lepple, in Graham and Duce 1979). This percentage was obtained after a contact time of 12 h, with a  $P_c \sim 60 \text{ mg L}^{-1}$  and a total phosphorus concentration in the aerosols of 0.2%. Herut et al. (1999b) established that 11% of the total phosphorus contained in loess particles ( $P = 0.04\%$ ) is released in surface seawater for a  $P_c$  of  $90 \text{ mg L}^{-1}$ . From our experiments in seawater, the percentage of dissolved phosphorus ( $D_{sw}$ ) appears to be closer to 3% for a  $P_c$  of  $60 \text{ mg L}^{-1}$  and 2% for a  $P_c$  of  $90 \text{ mg L}^{-1}$ . These percentages are lower than those determined by Lepple and Herut, and this is probably due to differences in concentration of total phosphorus and differences in the types of dust. The  $P_c$ s used in Lepple's and Herut's experiments in seawater are not representative of the particle concentrations encountered in surface seawater after a Saharan event due to an important dilution effect. In our approach, the minimum  $P_c$  used was  $5 \text{ mg L}^{-1}$ , and this value can be considered the maximum particle concentration that can be found in the first meter of seawater after a Saharan event of high magnitude.

*Comparison of the dissolution of Saharan phosphorus in rainwater and seawater*—The same type of curves found in ultrapure water experiments were found in DIP-free seawater. From our experiments, the percentages of dissolved phosphorus were higher, for an equivalent  $P_c$ , in Saharan rainwater than in seawater (Fig. 7). For example, after a contact time of 24 h, the percentages of DIP for a  $P_c$  of  $5 \text{ mg L}^{-1}$  were 21% and 12% in ultrapure water and seawater, respectively. Consequently, there is no significant additional dissolution of phosphorus in seawater after particles have been in contact with a significant amount of rainwater. However, some of the Saharan events carry very significant amounts of dust with only few drops of rainwater. In this case, the raindrops are evaporated immediately, and the rainfall is not measurable. For these particular events, the dissolution in rainwater is very low, and the main dissolution process will occur in the seawater. This process may poten-

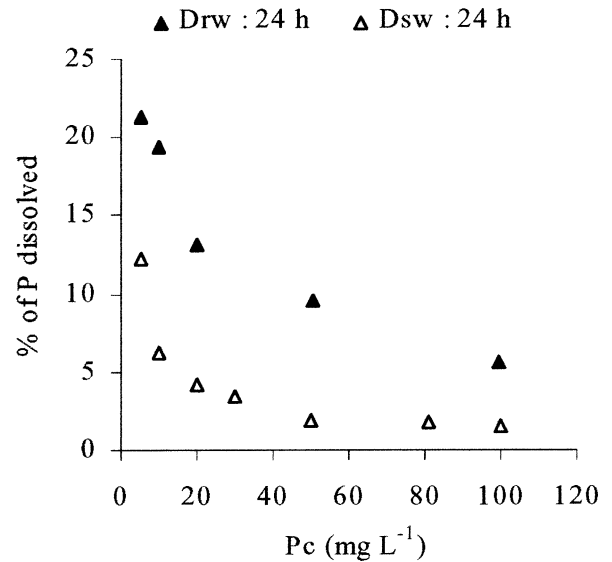


Fig. 7. Percentage of dissolved inorganic phosphorus in ultrapure water and seawater, as a function of the amount of Saharan dust introduced ( $P_c$ ,  $\text{mg L}^{-1}$ ) for a contact time of 24 h.

tially increase the contribution of Saharan inputs of phosphate in the global P budget in the Mediterranean.

*Results of the dissolution experiments applied to field data*—The relationships established from in vitro experiments describe the dissolution of phosphorus present in the Saharan aerosols as a function of the mass of particles in the rain and of the contact time between particles and raindrops. These relationships can be used to evaluate the flux of DIP associated with the Saharan source at annual and event time-scales. Results on dissolution in seawater will be applied to events that occurred with only small amounts of rainfall.

In 1999, 26 Saharan and “mixed” rains were collected at Villefranche-sur-Mer. The annual flux of Saharan matter measured was  $4.4 \text{ tons km}^{-2}$  for this year. Knowing the rainfall (denoted as “H,” expressed in  $\text{mm} = \text{L m}^{-2}$ ) and the weight of Saharan matter (in mg) for each rain, the particle concentrations ( $P_c$ , in  $\text{mg L}^{-1}$ ) were calculated. For each rain, the Saharan DIP flux was calculated by use of the relationships established from the in vitro experiments in ultrapure water. The power laws corresponding to two exposure times of particles in rain (10 min and 24 h) were used and the fluxes calculated as follows:

$$\begin{aligned}
 10 \text{ min: } \quad & \text{DIP}_{(\mu\text{M})} = 0.018 \times (P_c)^{0.498} \quad \text{and} \\
 & \text{DIP}_{(\mu\text{mol m}^{-2})} = \text{DIP}_{(\mu\text{M})} \times H_{(\text{L m}^{-2})} \\
 24 \text{ h: } \quad & \text{DIP}_{(\mu\text{M})} = 0.0241 \times (P_c)^{0.506} \quad \text{and} \\
 & \text{DIP}_{(\mu\text{mol m}^{-2})} = \text{DIP}_{(\mu\text{M})} \times H_{(\text{L m}^{-2})}
 \end{aligned}$$

The estimated DIP flux carried to the sea surface by Saharan rains varied from  $0.03$  to  $2.6 \mu\text{mol m}^{-2} \text{ rain}^{-1}$  (mean,  $0.6 \pm 0.6 \mu\text{mol m}^{-2} \text{ rain}^{-1}$ ). By summing the DIP fluxes obtained for all the rains for a year, a yearly DIP Saharan flux, associated with dissolution in rainwater, was estimated to be between  $0.4$  and  $0.5 \text{ kg km}^{-2}$  ( $12$  and  $16 \mu\text{mol m}^{-2}$ ) for

1999. It should be noted that this flux was probably underestimated for two reasons: (1) most of the time, Saharan rains are associated with anthropogenic particles, and the resulting pH can be lower than the one in the dissolution experiment with Saharan soil ( $\text{pH} \geq 5.5$ ), which leads to a possible increased dissolution of Saharan phosphorus; and (2) the Saharan particulate matter collected after filtration of the rain has lost a part of its mass because of the dissolution process of  $\text{CaCO}_3$  that occurred in the rainwater (in the relationships established experimentally between the DIP released and Pc, we used a concentration of particles that came from a soil and not from aerosols that had undergone a loss of mass because of the dissolution process in rainwater). This carbonate phase can represent 2%–20% of the rain particulate phase (Guieu et al. in press).

In 1999, six Saharan rains carried significant amounts of dust with only few drops of rainwater. In this case, the main dissolution process occurred in the surface seawater. To evaluate the inputs of Saharan DIP in seawater, the results from dissolution experiments in seawater had to be extrapolated. For a low Pc ( $5 \text{ mg L}^{-1}$ ),  $D_{\text{sw}}$  reached 10%–15% (Fig. 6), but when the dust entered the seawater, the dilution effect led to very low dust concentrations ( $\ll 5 \text{ mg L}^{-1}$ ). We assumed that, in seawater, the dissolution percentage was at least of the same order of magnitude as the dissolution percentage established experimentally for a Pc of  $5 \text{ mg L}^{-1}$ ; therefore, a range of dissolution percentages from 10% to 15% (of the total phosphorus) was applied. For each event, the estimated Saharan DIP inputs associated with the dissolution in seawater varied from 0.6 to  $2.3 \mu\text{mol m}^{-2} \text{ rain}^{-1}$ . By summing the DIP fluxes obtained for all the events for a year, a yearly DIP Saharan flux was estimated to be between 0.2 and  $0.3 \text{ kg km}^{-2}$  (6 and  $9 \mu\text{mol m}^{-2}$ ) for 1999. The total atmospheric Saharan DIP flux (dissolution in rainwater and in seawater) was estimated to  $0.6\text{--}0.8 \text{ kg km}^{-2}$  ( $18\text{--}26 \mu\text{mol m}^{-2}$ ) for 1999. The DIP flux associated with the dissolution in seawater represented ~35% of the total atmospheric Saharan DIP flux. This highlights the significant role of these particular Saharan events, which are associated with only few drops of rainwater, in the annual flux of atmospheric Saharan phosphate. The Saharan dust thus represents a source of atmospheric phosphate to the western Mediterranean waters.

#### Impact of a Saharan dust event on primary production—

From June through the end of October 1999, during the oligotrophic period, 11 Saharan rains occurred at Villefranche-sur-Mer: 2 in spring, 5 in summer, and 4 in autumn. These rains were collected, and their characteristics are presented in Table 4. The air mass trajectories indicated a direct transport of mineral particles from North Africa, and some may be associated with polluted air masses. Some of these events carried very significant amounts of dust with only a few drops of rainwater (Table 4, samples labeled 1 and 3–6). In these cases, the raindrops evaporated immediately, and the rainfall was not measurable. For these events, the rainfall was chosen as 0.01 mm. The flux of Saharan particles for the 11 Saharan rains was within the range  $25\text{--}590 \text{ mg m}^{-2} \text{ rain}^{-1}$ . The dust deposition of these 11 events corresponds

Table 4. Characteristics of typical Saharan rains collected at Villefranche-sur-Mer from June to October 1999 and Saharan DIP fluxes (in  $\mu\text{mol m}^{-2}$ ) associated to each rain. The DIP fluxes were calculated according to the dissolution experiments in ultrapure water and seawater presented in this study. For the rains where only few drops were collected (rains "1," "3," "4," "5," and "6"), the main dissolution occurred in the seawater (dissolution percentage 10%–15%).

Rain labels	Date of collection (1999)	Rainfall (H in L m <sup>-2</sup> )	Weight of Saharan particles collected on filter (mg)	Flux of Saharan particles (mg m <sup>-2</sup> )	Concentration of Saharan dust in rain (Pc in mg L <sup>-1</sup> )	Estimated DIP flux carried by rainwater* (μmol m <sup>-2</sup> )	Estimated DIP flux corresponding to additional dissolution in seawater (μmol m <sup>-2</sup> )	Total estimated DIP flux per event (μmol m <sup>-2</sup> )
1	6 Jun	0.01	20.5	515	51508	0.04–0.06	1.3–2.0	1.4–2.1
2	10 Jun	3.8	8.7	219	57	0.5–0.7	—	0.5–0.7
3	19 Aug	0.01	19.9	500	50000	0.04–0.06	1.3–1.9	1.3–2.0
4	20 Aug	0.01	23.5	590	59045	0.04–0.06	1.5–2.3	1.6–2.4
5	21 Aug	0.01	8.9	224	22362	0.03–0.04	0.6–0.9	0.6–0.9
6	27 Aug	0.01	10	251	25126	0.03–0.04	0.6–1	0.7–1.0
7	19 Sep	68	2.6	65	1.0	1.2–1.6	—	1.2–1.6
8	13 Oct	4	1	25	6	0.2–0.25	—	0.2–0.25
9	20–21 Oct	53	6.5	163	3.1	1.7–2.3	—	1.7–2.3
10	24–25 Oct	110	1.0	25	0.2	0.9–1.3	—	0.9–1.3
11	30 Oct	0.9	21.5	540	600	0.4–0.6	—	0.4–0.6

\* Dissolution laws established in this study were applied: 1st number, contact time of 10 min and 2nd number, contact time of 24 h.

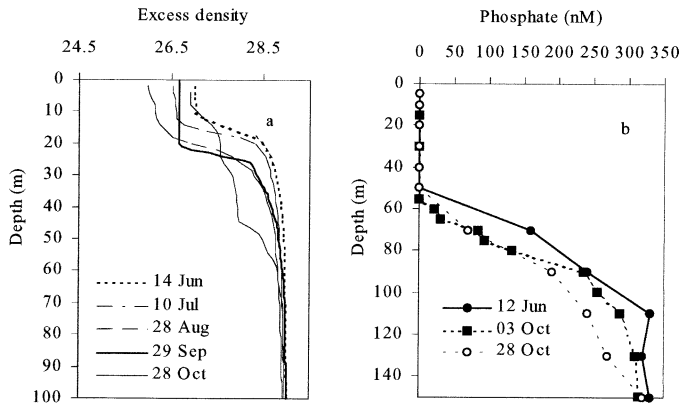


Fig. 8. (A) Excess density profiles as a function of depth (meters) in the western Mediterranean Sea (measurements at the DYFAMED station) during the oligotrophic period, for 1999. (B) Phosphate (DIP) profiles (nM) in the western Mediterranean (DYFAMED station) as a function of depth (m) during the oligotrophic period for 1999 (data available at <http://www.obs-vlfr.fr/jgofs2/sodyf/home.htm>). The measurements from 29 September and 3 October were taken during the PROSOPE campaign (<http://www.obs-vlfr.fr/jgofs/html/prosope/home.htm>).

to 3.1 tons km<sup>-2</sup>, which accounts for ~70% of the annual deposition of Saharan matter (4.4 tons km<sup>-2</sup> for 1999).

The DIP fluxes calculated from dissolution laws (at 10 min and 24 h) established in ultrapure water, ranged from 0.03 to 2.3  $\mu\text{mol m}^{-2} \text{rain}^{-1}$ , with an average of  $0.5 \pm 0.7 \mu\text{mol m}^{-2} \text{rain}^{-1}$  (Table 4). The coefficient of variation was very high, which illustrates the high temporal variability of the magnitude of Saharan pulses. These 11 Saharan rains brought 5–7  $\mu\text{mol m}^{-2}$  of DIP to the surface water between June and October, representing 42% of the annual input of DIP associated with Saharan rains (12–16  $\mu\text{mol m}^{-2} \text{yr}^{-1}$ ). For the rains associated with a significant amount of rainfall, there was no significant additional dissolution of phosphorus in surface seawater. By comparison, for the five Saharan rains associated with only few drops of rainwater, the release of DIP occurred mainly in seawater. For these particular events, the total DIP fluxes correspond to the sum of the DIP flux in the air column and in the seawater column (see Table 4). The DIP inputs established in seawater ranged from 0.6 to 2.3  $\mu\text{mol m}^{-2}$  (Table 4). These five particular Saharan events brought 5–8  $\mu\text{mol m}^{-2}$  of DIP to the surface water between June and October, which is the same order of magnitude as the DIP flux associated with the dissolution in rainwater during the same period (5–7  $\mu\text{mol m}^{-2}$ ).

From June through the end of October 1999, the surface waters are isolated from the intermediate and deep waters rich in nutrients. Consequently, the nutrient concentrations in the surface Mediterranean waters were, during this stratification period, “undetectable” by the analytical standard methods (<0.02  $\mu\text{M}$  for phosphate and <0.1  $\mu\text{M}$  for nitrate). During this period, at the DYFAMED station located in the central Ligurian Sea (43°25'N, 7°52'E), the surface layer was homogeneous in density (Fig. 8), the thickness of this layer varying from 10 m (June and October) to a maximum of 20 m (September). This layer was nutrient depleted, and the phosphocline, which was deeper than the nitracline

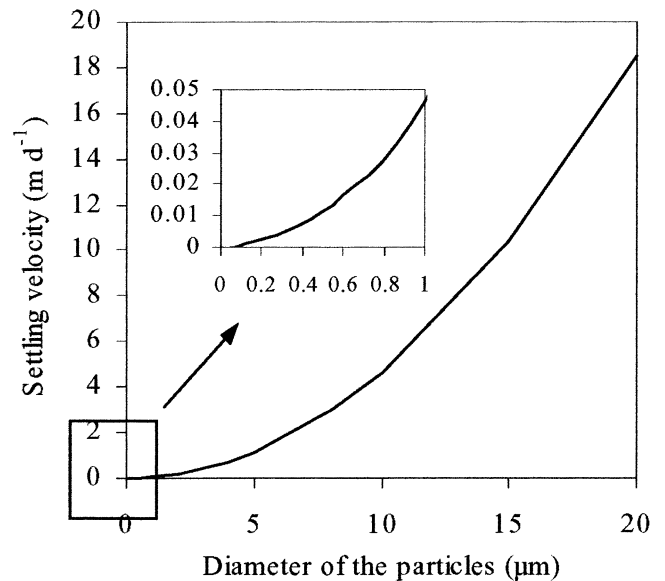


Fig. 9. Settling velocities of Saharan dust in seawater ( $\text{m d}^{-1}$ ) as a function of the diameter of the particles ( $\mu\text{m}$ ). The settling velocity is calculated from Stokes' law, under the assumption that the mean density of Saharan dust is  $2500 \text{ kg m}^{-3}$  (D'almeida and Schütz 1983).

(Moutin and Raimbault in press), ranged from 40 to 55 m in depth (Fig. 8). Thus, during this period, the biological activity was P-limited, as has been previously suspected for similar trophic conditions in Mediterranean Sea (Thingstad and Razzoulzadegan 1995; Vaulot et al. 1996; Thingstad et al. 1998), and the only external source of DIP for the mixed layer was the atmosphere.

The sedimentation rate of the Saharan particles in seawater can be computed as a function of particle size by use of Stokes' law (Fig. 9). It should be noted that this approach does not take into consideration horizontal and vertical water movements, grazing of particles by zooplankton, and aggregating mechanisms of particles in the surface layer. A size fraction <1  $\mu\text{m}$  (diameter) represents sedimentation rates that are very slow ( $\leq 5 \text{ cm d}^{-1}$ ). These fine particles represent up to 90% of the total number of Saharan aerosols (Chester and Johnson 1971). Consequently, these fine particles may accumulate in the surface layer during the entire stratified period and could potentially represent, in terms of DIP, a contribution to in situ production.

If we assume that all the DIP released from the Saharan particles is available to the biological community, and if the biological communities produce organic matter with a Redfield ratio C:P of 106:1, the production induced by each rain can be calculated through the following formula:

$$\begin{aligned} & \text{production induced by rain} \\ &= \frac{\text{total DIP flux}_{(\mu\text{mol m}^{-2})} \times 106 \times 12}{1000} \end{aligned}$$

This rain-induced production corresponds to new production as a result of atmospheric input of “Saharan DIP” and ranges from 0.2 to 3  $\text{mg C m}^{-2} \text{rain}^{-1}$ , totalling 13–19  $\text{mg C m}^{-2}$  from June to October (see Table 5). For this oligotrophic

Table 5. New production (NP) induced by an input of "Saharan DIP," expressed in  $\text{mg C m}^{-2}$ , during the oligotrophic period. Contribution (%) to the (1) in situ total integrated new production in the layer 0–90 m ( $20 \text{ mg C m}^{-2} \text{ d}^{-1}$ ), (2) to the in situ total primary production (PP) in the surface mixed layer at 0–10 m ( $22 \text{ mg C m}^{-2} \text{ d}^{-1}$ ) and (3) to the in situ total (PP) in the surface mixed layer at 0–20 m ( $40 \text{ mg C m}^{-2} \text{ d}^{-1}$ ). The F ratio calculated corresponds to the ratio of new production induced by "Saharan DIP" primary production (in the 0–10 and 0–20 m layers, respectively).

Rain labels	NP induced by Saharan DIP ( $\text{mg C m}^{-2}$ )	(1) % of the integrated NP <sub>0–90 m</sub> explained by "Saharan DIP"	(2) % of the PP <sub>0–10 m</sub> explained by "Saharan DIP"	(3) % of the PP <sub>0–20 m</sub> explained by "Saharan DIP"	F ratio induced by Saharan DIP in the surface mixed layers at 0–10 and 0–20 m
1	1.7–2.6	9–13	8–12	4–7	0.04–0.12
2	0.7–0.9	3–5	3–4	2	0.02–0.04
3	1.7–2.5	8–13	8–12	4–6	0.04–0.12
4	2.0–3.0	10–15	9–14	5–7	0.05–0.14
5	0.8–1.2	4–6	3–5	2–3	0.02–0.05
6	0.9–1.3	4–6	4–6	2–3	0.02–0.06
7	1.5–2.0	8–10	7–9	4–5	0.04–0.09
8	0.2–0.3	1–2	1	1	0.01
9	2.1–2.9	11–14	10–13	5–7	0.05–0.13
10	1.2–1.6	6–8	5–7	3–4	0.03–0.07
11	0.5–0.7	2–4	2–3%	1–2	0.01–0.03

period, it is interesting to compare these estimates of production induced by "Saharan DIP" with the direct measurements of productions, both at the scale of the entire oligotrophic period and at the event timescale.

In the first approach, the entire productive layer (0–90 m) was considered. In situ measurements of primary production (PP) were taken on a monthly basis by use of the standard  $^{14}\text{C}$  assimilation method at DYFAMED station (Marty and Chiaverini in press) at 10 different depths, ranging from 5 to 90 m. From June to October 1999, the primary production integrated over the 0–90 m water column was, on average,  $134 \pm 54 \text{ mg C m}^{-2} \text{ d}^{-1}$  (Marty and Chiaverini in press). The Fp ratio, defined by Claustre (1994) as the ratio of the integrated concentration of fucoxanthin and peridinin to the integrated concentration of pigments present in a phytoplankton community, is considered as an alternative to the f ratio (new production : total production; Eppley and Peterson 1979). The Fp ratio is, on average, 0.15 under oligotrophic conditions (Claustre 1994; Marty and Chiaverini in press), the new production (Fp ratio  $\times$  PP), from June to October 1999, integrated over the water column, can be estimated to be  $20 \text{ mg C m}^{-2} \text{ d}^{-1}$ . By assuming that there were no advective inputs, the "integrated" new production can be assumed to be the sum of (1) a new production induced by the atmospheric inputs of nutrients, (2) a new production induced by the diffusion of nutrients from deeper water, and (3) a new production induced by atmospheric  $\text{N}_2$  fixation by cyanobacteria. The new production induced by "Saharan DIP" for the entire oligotrophic season ( $13\text{--}19 \text{ mg C m}^{-2}$ ) was of the same order of magnitude as the total "integrated" new production per day ( $20 \text{ mg C m}^{-2} \text{ d}^{-1}$ ). As a result, the impact of "Saharan DIP" is negligible at the scale of the oligotrophic season. At the event timescale, however, the new production induced by "Saharan DIP" represented 1%–15% of the average new production integrated over the entire productive layer (see Table 5). For example, the rains "2," "5," "6," "8," "10," and "11" contributed <10% of the

new production, whereas rains "1," "3," "4," "7," and "9" contributed  $\sim 10\%$ – $15\%$  of the total new production integrated over the column water. If the biological activity is P-limited, new production induced by the atmospheric  $\text{N}_2$  fixation may be negligible. In this case, the new production can be essentially attributed to the vertical mixing.

In this second approach, only the surface mixed layer was considered: production induced by "Saharan DIP" was compared with production in the 0–10 and 0–20 m surface layers. The integrated primary production in the surface mixed layer 0–10 m and in the layer 0–20 m at the DYFAMED station were calculated. The primary production, during the oligotrophic period, averaged  $22 \text{ mg C m}^{-2} \text{ d}^{-1}$  for 0–10 m and  $40 \text{ mg C m}^{-2} \text{ d}^{-1}$  for 0–20 m. The Fp ratio, defined by Claustre (1994), is not adapted to estimation of the new production in the surface layer. The Fp ratio is calculated from concentrations of pigments specific to microphytoplankton (diatoms and dinoflagellates) (Claustre 1994), and these species are not abundant in the surface mixed layer during oligotrophic situation. The dominant species in the surface layer is cyanobacteria (*Synechococcus*) (Bustillos-Guzman et al. 1995; Marty and Chiaverini in press), a picophytoplanktonic species characteristic of oligotrophic systems. Thus, because the new production in the surface layer was not quantifiable, the new production induced by "Saharan DIP" was compared with the total primary production integrated over the mixed layer (Table 5). Under the assumption that there were no advective inputs and that vertical mixing and diffusion are negligible, we can postulate that the new production was due to (1) the atmospheric inputs of nutrients and (2) the  $\text{N}_2$  fixation by cyanobacteria. Again, new production induced by "Saharan DIP" over the entire oligotrophic season ( $13\text{--}19 \text{ mg C m}^{-2}$ ) was negligible compared with the daily total production in the surface layer ( $22$  and  $40 \text{ mg C m}^{-2} \text{ d}^{-1}$ ). At the event timescale, the contribution of the new production induced by the "Saharan DIP" to the surface primary production was highly variable from one event to another

but still represented up to 14% of the total phytoplanktonic production in the mixed layer. This result is consistent with the fact that, in the surface layer, the biological production was dominated by regenerated production during the oligotrophic situation. The F ratio (new production induced by Saharan DIP:total primary production in the surface layer) can be roughly estimated. This ratio (Table 5) ranged from 0.01 to 0.14 in the 0–10 m surface layer and from 0.01 to 0.07 in the 0–20 m surface layer.

During the oligotrophic season, the dominant species among the cyanobacteria in the surface waters in the western Mediterranean is *Synechococcus*. This species seems to be able to fix atmospheric nitrogen (Duerr 1981; Mitsui et al. 1986; Sachs and Repeta 1999) if the system is not P-limited. N<sub>2</sub> fixation may be very low during the period when DIP is depleted in the mixed layer, the only source of phosphate being the regenerated one. During a Saharan event, additional DIP might increase N<sub>2</sub> fixation. This hypothesis is in strong agreement with the findings of Bonin et al. (1989) which indicate that N<sub>2</sub> fixation seems to increase when the system is no longer P-limited, but, at the present time, this was not experimentally demonstrated. On the other hand, Saharan inputs also provide other dissolved components of biological significance such as iron (Sarhou and Jeandel 2001; Guieu et al. in press), which play significant roles in the fixation of atmospheric nitrogen by marine organisms (Falkowski 1997; Hood et al. 2000; Wu et al. 2000).

The new production induced by an input of “Saharan DIP” is low compared with the total production, but this input can potentially have some consequences on the marine ecosystem at different trophic levels. In this framework, incubations of oligotrophic Mediterranean seawater with Saharan dust have been performed recently (PROSOPE campaign, September 1999). This ongoing research has clearly shown that sporadic Saharan inputs lead to a biological response at bacterial and phytoplanktonic levels (Ridame and Guieu 2000; Ridame et al. unpubl. data).

Dissolution experiments have allowed us to improve on existing knowledge of the dissolution of Saharan phosphorus in rainwater and seawater. In the air column, the percentage of phosphorus that dissolves ranges from 1% to 21% and is a function of two parameters: the magnitude of the Saharan event (Pc) and the duration of contact between particles and rainwater in the air column. There is no significant additional dissolution of phosphorus in seawater after particles have been in contact with a significant amount of rainwater. However, some of the Saharan events carry very significant amounts of dust with only few drops of rainwater. For these particular events, the dissolution in rainwater is very low and the main dissolution process will occur in the seawater (percentage of dissolution ~10%–15%). On the basis of the results of our dissolution studies, the total atmospheric “Saharan DIP” flux (dissolution in rainwater and seawater) is estimated at 0.6–0.8 kg km<sup>-2</sup> (18–26 μmol m<sup>-2</sup>) for 1999. These sporadic Saharan events represent a significant source of phosphate (DIP) to the surface water of the western Mediterranean Sea.

By applying the Redfield ratio to the annual atmospheric “Saharan” DIP flux, the potential yearly carbon production was estimated for 1999 to be 23–33 mg C m<sup>-2</sup> yr<sup>-1</sup>, which

is negligible when compared with the annual primary production of 86 g C m<sup>-2</sup> yr<sup>-1</sup> at the DYFAMED station for 1999 (Marty and Chiaverini in press). The Fp ratio was estimated to be 0.22 for the same year (Marty and Chiaverini in press). Consequently, the annual new production was estimated to be ~19 g C m<sup>-2</sup> yr<sup>-1</sup> for 1999. The input of “Saharan DIP” contributed only 0.1%–0.2% of the annual new production. The impact of “Saharan DIP” is, thus, negligible at a global or annual scale for the biological production. Additionally, when considering the entire oligotrophic period (June–October), the new production induced by the input of “Saharan DIP” (13–19 mg C m<sup>-2</sup>) was of the same order of magnitude as the total integrated new production per day (20 mg C m<sup>-2</sup> d<sup>-1</sup>), which indicates that the impact of “Saharan DIP” is negligible at this scale. However, at the event timescale and during the oligotrophic period, the new production induced by “Saharan DIP” can represent up to 15% of the total integrated new production and up to 14% of the primary production in the mixed surface layer. In this case, an input of “Saharan DIP” may stimulate in situ production directly or enhance atmospheric N<sub>2</sub> fixation.

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