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Chemical characterization of the Saharan dust end-member: Some biogeochemical implications for the western Mediterranean Sea

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[1] Two types of samples were used to chemically characterize the Saharan end-member: fine fractions of surface soil samples collected in Northern Africa and particulate phases of typical Saharan rains. Since the concentrations measured in the particulate phase of the Saharan rains were corrected from the dissolution losses in rainwater, these particles were considered to be representative of the transported Saharan dust before being blended into rainwater. Al, Fe, P, and Pb were analyzed: except for lead, the chemical composition of the transported Saharan dust was more homogeneous than the composition of individual soils. As confirmed by the air mass back trajectories, the higher level of homogeneity of the aerosol is partly due to the fact that a dust event affects a large area of the Saharan desert, and the composition of the particles reflects the average composition of the eroded areas. Pb concentration in the transported dust reflected an anthropogenic fraction. By using Pb/Al measurements from the soils it was shown that a typical Saharan rain event with no mixing with air masses from Europe appears to be very rare in the Mediterranean environment. The following values are proposed to characterize the Saharan dust end-member: Al (%) = 7.09 ± 0.79 ; Fe (%) = 4.45 ± 0.49 ; P (%) = 0.082 ± 0.011 ; Pb (ppm) = 24 ± 9 . This study suggests that the [element/Al or Fe] ratio is also useful to characterize the Saharan end-member as they are very homogeneous for the two sample types. Saharan dust represents a potential source of nutrients (P, Fe) for the Mediterranean water. Indeed, it accounts for ~30–40% of the total atmospheric flux of phosphorus in the western Mediterranean, and it governs the biogeochemical cycle of iron being the main source of dissolved iron in the western Mediterranean waters. INDEX

TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 3655 Mineralogy and Petrology: Major element composition; 3670 Mineralogy and Petrology: Minor and trace element composition; 4808 Oceanography: Biological and Chemical: Chemical tracers; 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; KEYWORDS: aluminum, iron, lead, phosphorus, Mediterranean Sea, Sahara

1. Introduction

[2] Desert dust is a source of mineral aerosols, whose geological and biogeochemical impacts are now recognized [Prospero, 1981; Chester, 1986; Pye, 1987; Duce *et al.*, 1991; Duce and Tindale, 1991; Jickells, 1995; Gao *et al.*, 1997]. The climatic role of desert dust [d'Almeida, 1989; Andreae, 1996; Li *et al.*, 1996; Tegen *et al.*, 1996] is an important question in the crucial debate on global change. 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 [Duce *et al.*, 1991; Ridame and Guieu, 2002; Jickells and Spokes, 2000; Fung and Doney, 2000].

[3] For the Mediterranean and North Atlantic regions the Saharan desert is the source of mineral dust. In the Mediterranean many studies have described the occurrence of Saharan dust events, the mineralogical properties of Saharan dust and emphasized its geological and biogeochemical roles [see e.g., Loyé-Pilot *et al.*, 1986; Chester *et al.*, 1996; Guieu *et al.*, 1997; Guerzoni *et al.*, 1999; Ridame and Guieu, 2000]. However, there is a lack of an adequate reference when it comes to tracking the terrigenous source among the different aerosol sources (marine, volcanic, anthropogenic) in the Mediterranean atmosphere and checking the strength

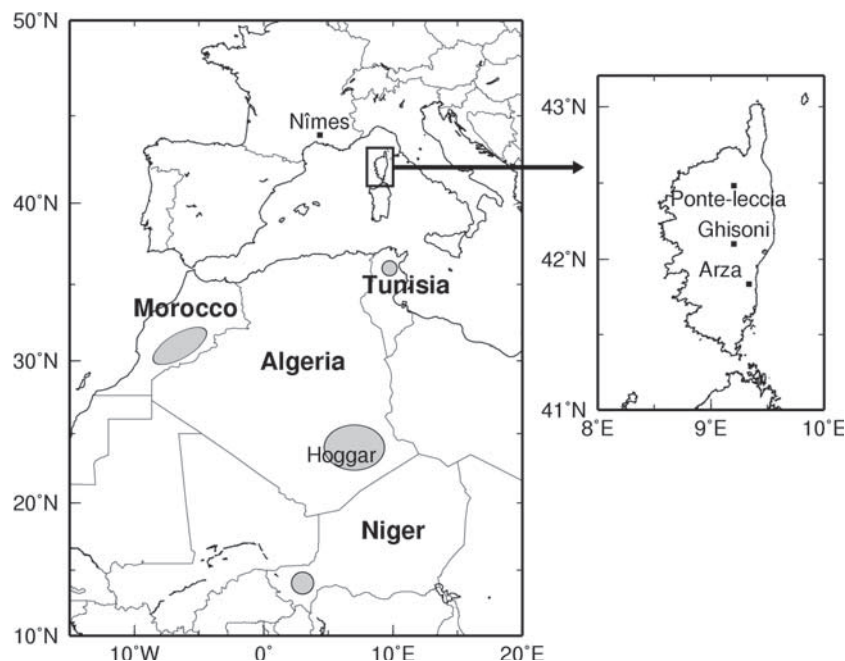


Figure 1. Location of the sampling sites (North Africa, soil samples; Corsica, rain samples; south of France (Nîmes), one rain sample).

of the natural sources versus the anthropogenic ones. In the literature, authors refer more often to crustal concentrations, or to the mean composition of the upper crust as given by various authors [Taylor, 1964; Taylor and McLennan, 1985; Mason, 1982; Wedepohl, 1995]. However, Saharan dust is derived from arid soils, alluvial fans, or ancient argillous formations, 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 [Mason, 1982; Martin and Withfield, 1983]. A better reference for mineral sources of aerosols would be the mean composition of soils or silt sediments, which are the result of soil erosion, as described by Martin and Withfield [1983]. A further fractionation occurs when dust is generated from loose surface soils. The uplifted dust has a lower grain size than the parent material and is enriched in the clay fraction, which produces a mineralogical, then chemical fractionation [Rahn, 1976; Schütz and Seibert, 1987; Sabre *et al.*, 2000]. Consequently, a correct reference should be looked for in the fine fraction of Saharan soils or in the dust itself. The composition of dust is often documented on the northern part of the Mediterranean, where a contamination by mixing with anthropogenic components in the atmosphere is possible [Guieu and Thomas, 1996].

[4] The aims of this paper are to examine the question of the chemical composition of the Saharan dust end-member in order to get (1) an adequate reference to assess the contribution of this source in the composition of the Mediterranean atmosphere and atmospheric deposition and (2) a correct assessment of the composition of that end-member in elements of high biogeochemical significance like iron and phosphorus.

[5] These points are discussed for the western Mediterranean only, as the dust source zones for the Eastern

Mediterranean are different [Guerzoni *et al.*, 1999] and include some contribution from the Arabian Desert.

[6] The elemental composition of the particulate phase of selected “Saharan rains” collected at the northern border of the Mediterranean coast and of the fine fraction of Saharan soils was established and compared in order to present a realistic mean composition of the Saharan end-member. Only a few elements of biogeochemical significance were analyzed: Al as a tracer of the crustal origin of aerosols; Fe and P as potential nutrients to the marine waters and Pb as a tracer of the potential anthropogenic contamination occurring during Saharan aerosol transport and fallout.

2. Material and Method

2.1. Soils Samples

2.1.1. Collection

[7] Surface soil samples were collected from various source regions of the Saharan aerosol using clean sampling techniques. Remote sites were chosen to be isolated from any highway or road dust influence: samples were primarily collected by traversing large, flat areas. Soils were collected manually with powder-free polyethylene gloves and stored in double plastic bags. In total, thirteen samples, originating from various source regions, were collected (Figure 1). Nine samples were collected over southern Morocco and one in Tunisia, representing the Southern Maghreb source zones. One composite sample was collected from the Hoggar region, representing the central Saharan sources (this sample is actually a composite of 12 soils; see Guieu and Thomas [1996] and Ridame and Guieu, 2000]. Two samples were collected in Niger, from the Sahelian source zone.

2.1.2. Grain size separation

[8] According to various authors, between 80 and 90% of the Saharan aerosol mass undergoing long-range transport

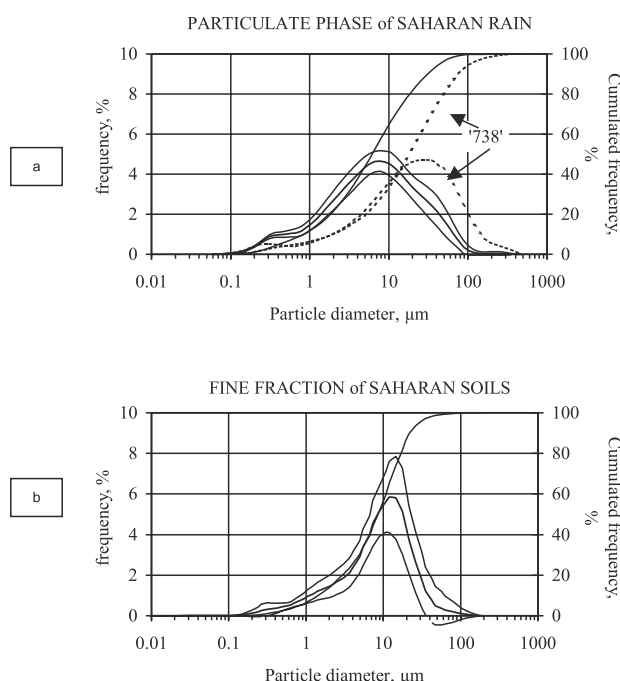


Figure 2. Grain size distribution in volume: frequency (thick solid line: mean; fine solid lines: 1σ) and cumulated frequency (average): (a) average size distribution of the particulate phase of six Saharan rains along with the distribution of the sample 738; this sample was separated from the rest of the data set because its distribution was quite different. (b) Fine fraction of Saharan soils (seven samples).

belongs to the 20- μm diameter and below size-fraction [Bücher and Lucas, 1975; Bücher et al., 1983; Delany et al., 1967; Schütz and Seibert, 1987; Guerzoni et al., 1992; Molinaroli et al., 1993; Kiefert et al., 1996]. To be as representative as possible of the wind-transported material, the soils were dry hand-sieved through successive polyethylene meshes (100 and 20 μm). The fraction passing through the 20- μm mesh was collected and stored in acid-washed bottles. The proportion of the fine fraction of these

soils was found to be highly variable. Consequently, the final amount of fine particles was not the same for all the soils, and some parameters, such as the grain-size distribution, could not be performed for the whole sample set since the amount of fine material available at the end of the treatment was too small. Grain-size distributions were established for the fine fraction of seven soil samples (Figure 2b) dispersed in ultrapure water with a Mastersizer (Malvern Instruments, UK).

2.2. Particulate Phase of Selected Saharan Rain Events

[9] Ten samples were selected among a 12-year series collection [Lojé-Pilot and Martin, 1996] to be as representative as possible of pure Saharan events. It has been shown that the elemental composition in rainwater is highly dependent on the origin of the aerosol transported in the rain [Lojé-Pilot and Morelli, 1988; Lojé-Pilot et al., 1990]. According to criteria established by these authors, the selection of the Saharan events was based on (1) microscopic observation of the particulate phase, (2) composition in major elements under dissolved phase and pH, and (3) weight of particles collected. The samples were collected at three different sites in Corsica (Figure 1): Arza, Ghisoni, and Ponte Leccia. Samples were collected using a bulk plastic device (Standard rain gauge by Météo France) having a 400- cm^2 collection surface and situated 1.7 m above ground level. The collection was performed on a per event basis. Rain samples were filtered immediately after the end of the rain event through pre-weighted Nuclepore membranes (0.4- μm pore diameter, 47 mm). The weight of particulate material was obtained by weighing the filters, once dried. These events correspond to mass fluxes ranging from 0.3 to 3 tons of dust per square kilometer. In addition, another sample, collected near Nîmes (France) was also analyzed. The information concerning these samples is grouped in Table 1. Grain-size distributions were established for seven samples of the particulate phase of Saharan rains (Figure 2a): an aliquot of filter was taken, and the particles were removed and transferred in a plastic vial. For some samples of low dust weight, the grain-size distribution could not be performed.

2.3. Acid Digestion and Analysis of the Samples

[10] Aliquots of the samples (~ 20 mg) were acid digested inside a Milestone 1200 Mega microwave oven with 4 mL of

Table 1. Characteristics of the Saharan Rain Events Selected for This Study

Sampling Site (see Figure 1)	Sample Label	Date of Collection	Rainfall, mm	pH	Saharan Dust Collected on the Filter		Saharan Dust Associated to Each Event $\text{mg}\cdot\text{m}^{-2}$
					Measured Weight, mg	Actual Weight, ^a mg	
Arza	153	05-12-85	1.0	6.50	31	32.0	800
Nîmes	738	03-24-91	—	5.78	—	—	—
Ghisoni	883	12-06-87	15.0	6.80	96.1	109.3	2733
Ghisoni	598	04-25-89	4.0	—	43.3	46.8	1169
Pte Leccia	1246	10-14-93	1.4	7.07	46.4	47.4	1184
Pte Leccia	1248	10-17-93	few drops	nd	95.6	98.9	2472
Pte Leccia	1284	09-20-95	13.0	7.26	51.8	60.0	1499
Pte Leccia	1611	09-12-96	13.1	7.15	24.9	28.7	717
Pte Leccia	1612	09-12-96	4.7	7.03	11.2	12.6	315
Pte Leccia	1613	09-12-96	11.0	7.97	33.1	38.2	954

^a The total weight is the actual weight of Saharan dust prior to the dissolution of calcium carbonate; it was computed by adding the amount of CaCO_3 that have been dissolved in the rain or in the DIW used for the collection. This calculation was made by using the elemental composition of the dissolved fraction (not shown).

HNO₃ (suprapur); 6-mL H₂O were added to the digested sample. Aliquots were then diluted according to the analytical technique used; the acid digestion protocol is fully described in *Ridame* [1997]. Ten aliquots (9.9–38.2 mg) of MESS-2 (a sediment reference material, National Council of Canada, widely used in trace metal geochemistry to validate acid digestion protocols) were digested inside the microwave oven to test the reliability of the acid digestion. Reagent blanks were performed to test the contaminant effect of the nitric acid used for the digestion. The digested samples were analyzed using a graphite furnace atomic absorption spectrometer (Varian AAS 800 Spectra) for Pb, by ICP-AES (JY 138 “Ultrac,” Jobin-Yvon, France) for Al and Fe and by the colorimetric method of *Murphy and Riley* [1962] (manual spectrophotometer (Anthelie Data)) for total phosphorus, adapted for the analysis of this type of sample [*Ridame*, 2001]. In all cases the concentrations were calculated from calibration curves. Blanks (reagent alone and reagent + blank filter) were below the detection limit. Results obtained on the certified reference material indicated a good accuracy of the analyses: the mean recovery for Al, Fe, Pb, and PO₄³⁻ were, in percentage, respectively 94 ± 6 , 108 ± 6 , 104 ± 6 , and 100 ± 7 . The low standard deviations (within about $\pm 6\%$) demonstrated a good reproducibility of results.

3. Results

3.1. Grain Size Distribution in Volume

[11] The average volume grain size distribution (frequencies of each class of size and cumulated frequencies) are presented for the two types of samples (fine fraction of soils and particulate phase of rains) in Figures 2a and 2b. The distribution in volume was mainly bimodal for the two types of samples: the first mode, similar for the whole data set, was situated at $\sim 0.3 \mu\text{m}$, but this fraction represented less than 1% of the total volume of the particles. The second mode was very similar for the soil samples and the particulate phase of the Saharan rains, on average between 10 and 20 μm . For the particulate phase of the Saharan rains the pattern of the distribution was “smoother,” with a third coarse mode for some samples. In one case, rain sample 738, this coarser mode was the main one. This coarser mode was already observed by *Guerzoni et al.* [1992] for some high-loaded dust samples from Sardinia. The cumulated frequencies established for the soils and the particulate phase of the red rains, indicated that the median was around 8 μm , except for the rain sample 738 for which it was around 20 μm .

[12] On the whole, the distributions were quite similar, showing that this fine fraction of the soils is a suitable representation of their “eolisable” component. In an attempt to convert these volume distributions into number distributions, a simple calculation was computed assuming that the particles were spherical. Even if this assumption is caution to critics, it clearly indicated that most ($\sim 100\%$) of the particles were smaller than 1 μm . This is in strong agreement with *Chester and Johnson* [1971] and *d’Almeida* [1987], who observed that, in Saharan aerosol, 60–90% of the total number of particles are smaller than 1 μm .

3.2. Air Mass Back Trajectories

[13] Three-dimensional, 4-day air mass back trajectories calculated by Météo France were established for the ten rain

events considered in the present study (Figure 3). The operational model of Météo France has been improved by *Martin et al.* [1987] and validated for the transport of Saharan dust by *Martin et al.* [1990]. These trajectories were calculated for two atmospheric end levels (700 and 850 hPa) in order to determine if the air masses were originating from the same region at the different levels of the air-column. For all the samples the trajectories clearly indicated a transport from the Saharan regions; but for most of the samples the air masses did not exclusively originate from northern Africa for the two levels and during the whole rainy period. In fact, the meteorological situation can evolve very rapidly, and in a matter of a few hours, the air masses can originate from the northeastern Atlantic (for example, see trajectories for samples 1246, 1284, and 738) or even northern Europe (trajectories for sample 883). For one sample (1611) the trajectory at level 700 hPa originated from Algeria, whereas at 850 hPa it was originating from southwestern France.

[14] These samples were carefully selected among a 12-year series collection and from visual observation. The analysis of major elements, the pH value, and the amount of dust collected were strong candidates to represent pure Saharan events. In fact, the observation of the air mass back trajectories at two pressure levels showed that pure Saharan events are very rare and thus difficult to collect because the mixing of Saharan dust plumes with different air masses occurs most of the time in rain events.

[15] Another consequence of the rapid change in meteorological situations is the fact that the air masses contributing to one Saharan event sweep over large regions of North Africa, generally from Morocco to Tunisia. This is particularly well illustrated by the air mass back trajectories of the samples 1284, 598, 1248, 883, 1612, and 738.

3.3. Metals Concentrations and Phosphorus Content

[16] The concentrations of Al, Fe, Pb, and P are reported in Table 2. For the particulate phase of the Saharan rains the concentrations were recalculated, taking into account the loss of the particulate mass due to the dissolution of CaCO₃. The calculation was performed using the composition in major ions determined in the dissolved phase (not shown), and the dissolved Ca originating from the particulate carbonate initially present in the Saharan aerosol (gypsum being negligible) [*Loÿe-Pilot et al.*, 1986; *Loÿe-Pilot and Morelli*, 1988]. The calculation indicated that the carbonate phase represented from 2 to 20% of the mass of particles (Table 1). The corrected concentrations were thus lower than the concentrations initially found. This correction is not usually made, and the concentrations of metals reported for particulate matter of Saharan rains or for Saharan aerosols collected with meshes and retrieved by dispersion in deionized water are generally overestimated.

[17] In the case of phosphate it has been shown recently [*Ridame and Guieu*, 2002] that a significant percentage of dissolved inorganic phosphate can be released in rainwater. This percentage depends on the particle load of the rain. Since phosphate was not measured in the rainwater, the amount of phosphorus that had dissolved from the particulate phase was estimated from the total particle load collected for each rain. Using the relationships [% PO₄³⁻ dissolved = F (particles load)] established experimentally by *Ridame and Guieu* [2002], the total particulate phosphorus

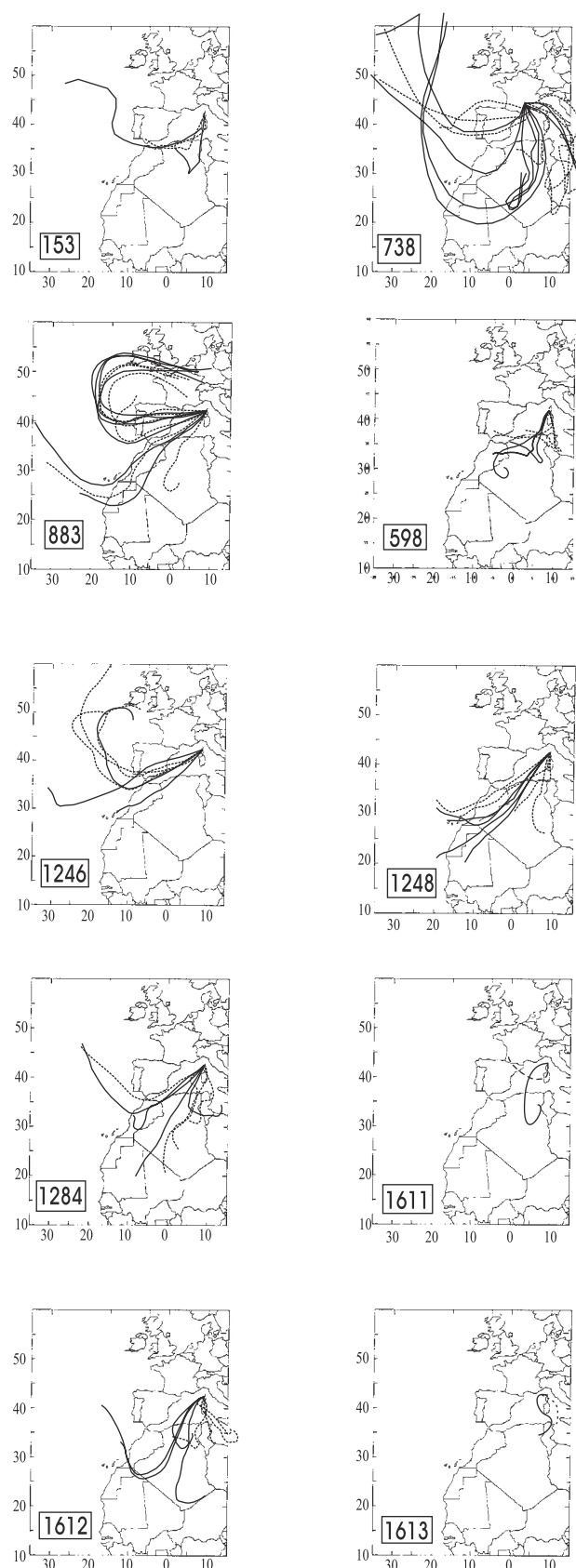


Figure 3. Three-dimensional, 4-day back trajectories, arriving at the sampling point for the rain samples (calculated by Météo-France). Dashed lines, ending point: 850 hPa; solid lines, ending point: 700 hPa.

was recalculated (Table 2): up to 13% of the particulate phosphorus (including all the particulate forms of phosphorus) had been dissolved in the rainwater. This type of correction was not applied for Al and Fe since the dissolution of these metals remains very low in Saharan rainwater [Guieu and Thomas, 1996] and does not affect the total concentration. Concentrations corrected from main dissolution processes will be considered in the following discussion as representative of the initial Saharan dust before its blending with rainwater. We should note that this correction from dissolution process only arises because we collected bulk rain and filtered it as opposed to conducting a total analysis of rainwater or aerosol.

[18] The average concentrations in Saharan dust and in the fine fraction of soils are reported in Table 3. For Al, Fe and P the chemical composition of the dust was much more homogeneous than the composition of the individual soils: variation coefficients around 10% for the rains against 25–40% for the soils. Lead concentrations were highly variable in both the soils and dust (variation coefficient around 40 and 30% respectively), the average concentration being much lower in the soils (around a factor of two).

4. Discussion

4.1. Variability of the Chemical Composition

[19] The concentrations in the transported dust were more homogeneous than in the fine fraction of the sampled soils. The higher level of homogeneity of the dust corresponds to the fact that, during a Saharan event that affects a large area of the Saharan desert, the composition of the particles reflects the average composition of the eroded areas [Bergametti, 1987; Schütz and Seibert, 1987; Pye, 1987]. This is quite well illustrated by the examination of the air mass back trajectories (Figure 3) of the events studied here. For example, a careful examination of the trajectories associated with event 1248 can be performed; a very high dust flux was associated with this event since the dust was deposited by only a few drops of rain during the night of 16 to 17 October 1993. The three-dimensional, 4-day back trajectories, arriving at the sampling point at 0000 and 1200 UT on 17 October at levels 850 and 700, showed that the air flux originated from northern Africa. The air mass swept across large areas from the west (Morocco) to the east (Tunisia), and thus the aerosols carried by the air masses may have been a mixture of ground particles that originated from Morocco, Mauritania, Algeria, and Tunisia. On the other hand, the soils are submitted to a continuous cycle of deflation, transport deposition, and resuspension [Schütz, 1989]; these phenomena lead to a relative homogeneity of the wind-transported material, but also of the elemental concentrations among the different soils samples. However, the signature of the local bedrock may still remain visible, explaining the differences observed between the different samples, as already mentioned by other authors [Coudé-Gaussen *et al.*, 1987; Bergametti *et al.*, 1989; Molinaroli, 1996; Avila *et al.*, 1998a; Chiapello *et al.*, 1997; Caquineau *et al.*, 1998]. The chemical composition of the transported dust was remarkably constant for Al, Fe, and P (variation coefficient 11–13%). For these reasons, the transported Saharan dusts were more representative of the Saharan end-member, in the case of Al, Fe, and P, than the studied soils.

Table 2. Chemical Composition of the Saharan Dust and of the Fine Fraction of Saharan Soils Along With Data From Literature^a

	Sample Label	Al, %	Fe, %	Phosphorus, %	Pb, ppm	
Particulate Phase of Rains, Corrected From Dissolution Losses = Saharan Dust, This Study						
				(a)	(b)	
	153	7.0	4.2	0.078	0.080	80
	738	7.8	5.1	0.079	0.079	42
	883	6.0	3.8	0.090	0.094	57
	598	8.3	5.1	0.098	0.102	68
	1246	6.3	4.0	0.075	0.078	40
	1248	6.0	3.8	0.062	0.064	26
	1284	7.6	4.8	0.083	0.089	50
	1611	7.5	4.6	0.065	0.074	42
	1612	7.5	4.7	0.069	0.077	42
	1613	7.0	4.4	0.074	0.081	39
Soils (< 20 μm), This Study						
Morocco	1	5.9	4.1	0.105		22
	2	9.5	5.7	0.064		24
	3	3.7	2.6	0.049		9
	4	7.0	4.5	0.085		42
	5	7.5	4.6	0.059		31
	6	5.8	3.9	0.047		26
	7	4.1	2.8	0.106		12
	8	5.8	3.6	0.065		34
	9	4.1	2.8	0.036		20
Algeria (Hoggar)	10	7.1	5.0	0.125		22
Niger	11	5.8	4.4	0.062		21
	12	4.9	4.0	0.059		18
Tunisia	13	4.1	3.2	0.070		26
Particulate Phase of Saharan Rains: From the Literature						
Avila et al. [1998]		24.1	4.4	0.107		64
		7.1	4.0	0.046		-
		22.5	3.7	0.059		31
		6.1	3.3	0.066		35
Bucher et al. [1975*, 1983 [£] , 1989]		3.1	1.6	0.022		59
		9.4	4.9	0.130		400 [£]
		8.6	4.7	0.060		-
		8.7	2.9	-		50*
Coudé-Gaussen [1987]		5.8	4.2	-		-
		6.9	3.6	-		-
		5.5	4.0	-		-
Guieu [1991], Values Corrected From the Carbonate Dissolution		5.3	3.7			160
		4.8	3.5			91
		6.0	4.1			57
Saharan Particles: Coarse Fractions						
Tomadin et al. [1984]	(collected on meshes)	8.2	5.6	0.080		-
		6.8	3.7	0.180		-
Guieu and Thomas [1996]	soils: fraction < 50 μm	7.4	4.6	0.360		26
Herut et al. [1999]	soils: fraction < 63 μm	3.4	2.3	0.039		-
Crustal References						
Mason [1982]	upper crust	8.1	5.0	0.105		13
Martin and Withfield [1983]	erodible crust	6.9	3.6	0.061		16
Taylor and Mc Lennan [1985]	upper crust	8.0	3.5	0.105		-
Wedepohl [1995]	average composition of the upper crust	7.7	3.1	0.067		17

^aFor this study, the concentrations found in the particulate phase of Saharan rains were corrected from dissolution processes in order to better evaluate the concentrations in the Saharan dust: the carbonate dissolution was taken into account (except for 738 for which Ca⁺⁺ was not measured). For 1248, the rainfall was not measurable (only few drops), so the dissolution was considered negligible. For phosphorus, the potential dissolution in rainwater was also taken into account: the concentrations found in the particulate phase of the rains (column a) were recalculated (column b) according to the laws [% DIP = particles concentration] determined in Ridame and Guieu [2002].

[20] Aluminum is currently used as an indicator of the crustal origin in the aerosol composition. Rather than use the mean Al concentration in the Saharan end-member (Al (%) = 7.09 ± 0.79 ; Table 3), a better approach would be the use of the average Me/Al ratio, which eliminates the variability owing to different mineralogical compositions, mainly due to the variations in the concentrations of quartz and carbonates. The Fe/Al ratio was very homoge-

neous in both the soils and Saharan dusts analyzed in this study, with an average value of 0.67 ± 0.06 (Table 3 and Figure 4). The concentrations established for the particulate phase of Saharan rains in the literature are much more scattered than those of the present study: this may be due to the fact that the corresponding events were mixed events, not as “pure” as those studied here and/or that there was an important contribution of local input. In

Table 3. Mean Concentrations (± 1 sigma) of Al, Fe, P, and Pb in the Saharan Dust and in the Saharan Soils, Along With Ratios $\text{El}/(\text{Fe or Al})^a$

	Mean Concentrations		
	Saharan Dust	Saharan Soils	Saharan Dust End-Member
Al, %	7.09 ± 0.79 (11%)	5.78 ± 1.68 (29%)	7.09 ± 0.79 (11%)
Fe, %	4.45 ± 0.49 (11%)	3.94 ± 0.91 (23%)	4.45 ± 0.49 (11%)
P, %	0.082 ± 0.011 (14%)	0.072 ± 0.026 (36%)	0.082 ± 0.011 (14%)
Pb, ppm	48 ± 16 (33%)	24 ± 9 (37%)	24 ± 9 (37%)
Fe/Al	0.63 ± 0.02 (3%)	0.69 ± 0.07 (10%)	0.63 ± 0.02 (3%)
P/Al	0.012 ± 0.002 (15%)	0.013 ± 0.005 (41%)	0.012 ± 0.002 (15%)
P/Fe	0.018 ± 0.003 (15%)	0.019 ± 0.008 (40%)	0.018 ± 0.003 (15%)
Pb/Al	$6.85\text{E-}4 \pm 2.21\text{E-}4$ (32%)	$4.15\text{E-}4 \pm 1.29\text{E-}4$ (31%)	$3.41\text{E-}4 \pm 1.16\text{E-}4$ (34%)

^aThe values in italic are proposed to characterize the Saharan end-member. Read $6.85\text{E-}4$ as 6.85×10^{-4} .

addition, these data had not been corrected for a potential dissolution of a part of the particulate phase. In particular, data presented by *Avila et al.* [1998a] indicated a very large range in Al concentrations (3 to 24%) that may not have been representative of the average composition of the Saharan aerosol in the Mediterranean atmosphere. The concentrations determined in Saharan soils or loess found in literature [*Guieu and Thomas*, 1996; *Herut et al.*, 1999] are also scattered but their Fe/Al ratios are in strong agreement with the one found in this study. Fe/Al ratios found in “Saharan aerosols” are much more homogeneous and generally similar to those proposed in this study. For example, $\text{Fe}/\text{Al} = 0.63 \pm 0.06$ in four samples of Saharan aerosols collected over the Tyrrhenian Sea [*Chester et al.*, 1984]; $\text{Fe}/\text{Al} = 0.62 \pm 0.11$ for 18 Saharan events collected in Corsica [*Bergametti et al.*, 1989] (these data were not reported in Figure 5 as only the concentrations in ng m^{-3} were available).

[21] In addition to the data corresponding to Saharan particles, four crustal references are reported in Figure 4. Except for the Al value from *Martin and Withfield* [1983], Al concentrations are higher than the average concentration of the Saharan end-member proposed in this study. Moreover, their Fe/Al ratios, except that from *Mason* [1982], did not fit the relationship determined in this study for the

Saharan end-member. This is due to the fact that the composition of the entire Earth’s crust differs from the mean composition of surface rocks, which are enriched in carbonates and where weathered formations enriched in hydroxy radicals are found.

4.2. Lead

[22] Average concentrations of Pb in the Saharan transported dust (48 ppm) were significantly higher than in the fine fraction of the Saharan soils (24 ppm). In fact, natural lead in Saharan soils themselves could be influenced to a certain extent by the global anthropogenic perturbation as is the case for the ocean [see e.g., *Schaule and Patterson*, 1981]. It could also be influenced by pollution sources located in North Africa itself. This hypothesis was checked by determining isotopic composition on the labile and the residual fractions of one of the soil (soil sample 10 from Algeria; K. Tachikawa, unpublished data 2001). According to the authors, there was only a very small contribution of anthropogenic or adsorbed Pb on the surface of the particles, but it could not be stated if this contribution was from the global anthropogenic perturbation and/or regional contamination. Despite this uncertainty, the lead concentrations in soils may be the most representative of the concentration in the Saharan end-member. Thus we assume that an average

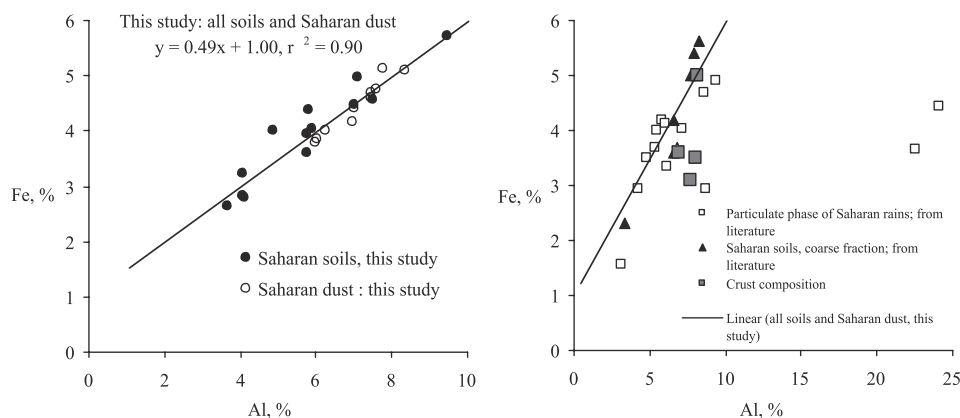


Figure 4. (left) Fe versus Al in fine fraction ($<20 \mu\text{m}$) of Saharan soils and in transported Saharan particles. (right) Fe versus Al reported from the literature (see data, Table 2): Saharan soils, coarse fraction [*Guieu and Thomas*, 1996; *Herut et al.*, 1999; *Tomadin et al.*, 1984]; particulate phase of Saharan rains [*Avila et al.*, 1998a; *Coudé-Gaussen*, 1982; *Ganor and Foner*, 1996; *Bücher and Lucas*, 1975; *Bücher et al.*, 1983; *Bücher*, 1989; *Guieu*, 1991]; crust composition [*Mason*, 1982; *Martin and Withfield*, 1983; *Taylor and McLennan*, 1985; *Wedepohl*, 1995].

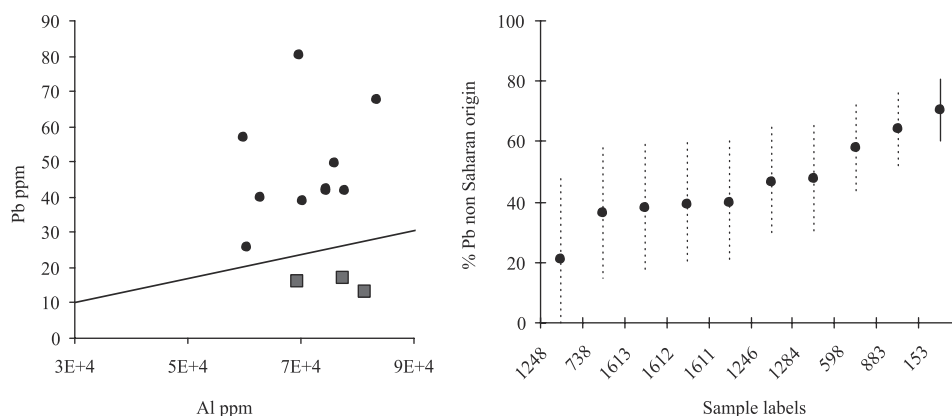


Figure 5. (left) Pb versus Al in the Saharan dusts (dots). The line represents the Pb/Al ratio in the Saharan end-member determined in this study (see text) and the squares represent the crust composition [Mason, 1982; Martin and Withfield, 1983; Taylor and McLennan, 1985; Wedepohl, 1995]. (right) Percentage of lead of non-Saharan origin in Saharan dust. This fraction in excess (Xs, in percent) was calculated as follows: $Xs = 100 - [Al_{sample} \times 3.41 \times 10^{-2} / Pb_{sample}]$.

Pb/Al ratio determined from the average Al concentration in the transported dusts and the average Pb concentration in the soils ($Pb/Al = 3.41 \times 10^{-4}$) was representative of the Pb/Al ratio of the Saharan end-member. There was no correlation between Pb and Al in the dusts and in most of these samples, Pb/Al ratios were higher than in the Saharan end-member, indicating the presence of lead of non-Saharan origin (Figure 5). By using the Saharan end-member ratio, the fraction of Pb of non-Saharan origin in the Saharan dusts collected far from the sources could be calculated (Figure 5). It should be noted that these selected “typical” Saharan rains actually have, to a certain extent, an anthropogenic component in spite of lead enrichment factors (Ef) close to 1 ($1.6 < Ef/Al < 3.4$). The corresponding percentage of Pb of non-Saharan origin varied from between 20 and 70% of the total lead. The percentage was minimal for sample 1248, for which the air mass back trajectory indicated a direct transport from different regions of Sahara (Figure 3). For several rains samples the average percentage was higher than 50%, indicating that a contamination occurred during the transport over the Mediterranean and/or that these rains were actually “mixed rains.” The 4-day back trajectories showed that both causes were involved to explain the enrichment. For example, in the case of sample 883 (60% of Pb of non-Saharan origin), the beginning of the event indicates unequivocally that air masses are coming from northern Africa; in a few hours the development of the depression centered on Europe caused the circulation of the air masses passing over Europe (Figure 3). For this sample the Pb in excess was probably due to anthropogenic components of the European aerosols. Samples 1612 and 1613 illustrate quite well examples of Saharan rains having both typical Saharan air mass trajectories mixed with air masses originating probably in the Mediterranean area (Figure 3). For these samples the non-Saharan component ($\sim 40\%$) could well illustrate what Chester *et al.* [1993] called “the Mediterranean anthropogenic-rich background.” On the other hand, this anthropogenic signature could also have originated in Europe from low-altitude air masses that had not been taken into consideration (the two altitudes considered in this study being 700

and 850 hPa) as evidenced by Bergametti [1987] and in the work of Martin *et al.* [1990].

[23] Data from the literature also indicate that the Pb/Al ratios in the particulate phase of Saharan rains are much higher than the Saharan end-member ratio, indicating that a significant fraction of Pb is of non-Saharan origin (Figure 5). In contrast, the ratio Pb/Al given for the average crust or the erodible crust is significantly lower, indicating that these references are not appropriate to characterize the Pb composition of the Saharan end-member. As previously mentioned by Ridame *et al.* [1999], the Sahara is a potential source of natural lead for the Mediterranean environment. Considering that the total atmospheric fluxes of Al and Pb to a remote site in Corsica were in 1995–1996 and 1996–1997 respectively: 171–270 and $1.1\text{--}0.7 \text{ kg km}^{-2} \text{ yr}^{-1}$ [Ridame *et al.*, 1999] and assuming that Pb/Al Saharan end-member = 3.41×10^{-4} (this study), the contribution of Saharan lead for these years represented 5–13% of the total lead flux. The limitation in the use of lead additives in gasoline may increase this proportion in the following years.

4.3. Biogeochemical Significance of the Input of Saharan Dust for the Mediterranean

[24] The establishment of the composition of the Saharan end-member allows us to assess the contribution of Saharan dust to the atmospheric input of elements of biogeochemical significance such as micronutrients.

4.3.1. Phosphorus

[25] Phosphorus seems to be a limiting factor of the primary production in the eastern Mediterranean [Krom *et al.*, 1991] and also during some periods in the western Mediterranean [Fiala *et al.*, 1976; Thingstad and Rassoulzadegan, 1995; Dolan *et al.*, 1995]. Most of the phosphorus in Saharan soil is present in inorganic form, and a large part of it is associated with iron oxyhydroxides coated on clay minerals and quartz particles, which give the Saharan particles their typical brown-reddish color. Average P/Fe and P/Al ratios in the Saharan soils and transported dusts are very similar (Table 3).

Table 4. Atmospheric Flux of Phosphorus to the Mediterranean: Contribution of the Saharan Source^a

	Feb. 1985 to Feb. 1986	Feb. 1986 to Feb. 1987	Unit
Total atmospheric flux of phosphorus	29.3	44.2	kg km ⁻² yr ⁻¹
Saharan dust flux	11.4	21.2	t km ⁻² yr ⁻¹
Phosphorus concentration in the Saharan end-member	0.082 ± 0.011	0.082 ± 0.011	%
Saharan flux of phosphorus	9.3 ± 1.2	17.4 ± 2.3	kg km ⁻² yr ⁻¹
Contribution to the total flux of phosphorus	30%	40%	

^aThe total atmospheric fluxes are from Bergametti [1987, and database available at <http://www.lisa.univ-paris12.fr>]; the Saharan dust flux are from Loÿe-Pilot et al. [1996].

[26] Only very few data exist on total deposition of phosphorus in the Mediterranean atmosphere. To our knowledge, only the study from Bergametti [Bergametti, 1987; Bergametti et al., 1992] reported total atmospheric fluxes actually measured. For the period February 1985 to February 1987 the Saharan dust flux was measured [Loÿe-Pilot and Martin, 1996]. Using the average concentration of phosphorus found in the Saharan end-member, the flux of phosphorus originating from Sahara origin was calculated (Table 4). Over these two yearly periods, the Saharan flux represented 30% to 40% of the total atmospheric flux of phosphorus. This is higher than the contribution calculated by Bergametti et al. [1992] (23% determined by using a P/Al_{crust} from Mason [1982]). A study is currently being carried out to evaluate the dissolved input of phosphorus originating from the Sahara to the Mediterranean and its biological impact on the surface waters [Ridame and Guieu, 2002].

4.3.2. Iron

[27] In a recent study [Ridame et al., 1999] the total atmospheric input of iron and aluminum (among other metals) was measured in Corsica over a period of 2 years. Using the Fe/Al ratio computed in the present study and assuming that all the aluminum present in the atmosphere was from the Sahara, the iron flux of Saharan origin was recalculated for the samples collected over the period. 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.

[28] Iron is an essential nutrient for phytoplankton growth [see, e.g., Sunda, 1988–1989]. 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, Guieu et al. [1997] proposed that the dissolved flux represented 4–17% of the total atmospheric flux of iron. In comparison to the other sources of dissolved iron in the western Mediterranean (Table 5), the atmospheric input of dissolved iron (4000–22,300 t yr⁻¹) predominates the inputs from the straits (4500–12,000 t yr⁻¹) and from the rivers (1000 t yr⁻¹) [Elbaz-Poulitchet et al., 2001]. 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 Pirio station in 1995–1997 was lower by a factor of 4–6 compared to the one measured at Cap Cavallo (Corsica) in 1987 [Bergametti, 1987] when high dust fluxes were also recorded in Corsica [Loÿe-Pilot and Martin, 1996]. This indicates that during the period of high dust flux (as was the case in the years 1986–1989), the budget of dissolved iron was even more dominated by the atmospheric inputs of Saharan origin. Concerning the anthropogenic source, if we consider that 4% of the iron flux is of anthropogenic origin (see above) and by applying a maximum dissolution percentage of 10% (measured at pH 3–4 in dissolution experiment, Guieu et al., 1993), the dissolved iron flux of anthropogenic origin would only represent 2 to 12% of the total atmospheric flux of dissolved iron. Atmospheric inputs from Sahara actually control the budget of total and dissolved iron and thus the potential biological impact of iron in the western Mediterranean.

[29] In the absence of any Saharan event during the summer stratification, as a first approximation, we can 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

Table 5. External Inputs of Dissolved Iron to the Western Mediterranean (Surface: 840 000 km²)

	Value	Source
<i>Atmospheric Input</i>		
Total iron flux, kg km ⁻² yr ⁻¹	118–156	Ridame et al. [1999]
Dissolved iron flux: percentage of the total flux	4–17	Guieu et al. [1997]
Dissolved iron flux, kg km ⁻² yr ⁻¹	5–27	
Input of dissolved iron to the western Mediterranean, t yr ⁻¹	4200–22,300	
Proportion of Saharan origin, %	96	from Fe/Al determined in the present study
<i>All External Inputs [from Elbaz et al., 2001] (w: Winter; s: Summer)</i>		
Atmosphere	4200–22300	
Rivers	1000	
	w	s
Gibraltar	630	1880
Sicily	11,300	2600
Total input	17,000–35,000	10,000–28,000

observed in the northwestern Mediterranean in May during a period of phytoplankton bloom [Sarhou and Jeandel, 2001]. In contrast, a succession of Saharan fallout events during the summer stratification in 1999 was followed by an increase of the dissolved iron concentrations in the surface waters (up to 2 nM in the mixed surface layer measured in September) [Guieu et al., 2002], which was directly available for the phytoplankton.

5. Conclusions

[30] Concentrations of major elements (such as Al and Fe) and minor elements (such as P) are more variable in soil samples collected in source regions of Saharan aerosols than in the transported Saharan dusts. Saharan dusts generally reflect the mixing of ground particles originating from various source regions and are thus more chemically representative than individual soils. However, the average Fe/Al, P/Al, and P/Fe ratios are very similar in the two types of samples and can be considered as representative of the Saharan end-member. The average Al, Fe, and P concentrations in the transported Saharan dust are considered as reference values for the Saharan end-member.

[31] Concerning lead, the higher mean concentrations of the transported dust as compared with soils reflects the contamination by anthropogenic components of mainly European origin. By using the average Pb/Al_{Saharan-end-member} ratio, a significant fraction of Pb (20–70%) was found to be of non-Saharan origin in the dusts collected in the northwestern Mediterranean. Typical Saharan rain events occurring without any mixing with polluted air masses appear to be very rare in the Mediterranean environment.

[32] The contribution of Saharan dust to the total atmospheric fluxes of Fe and P was calculated by using the ratios established in this study and represents 96 and 30–40% of their total deposition, respectively. The Sahara is a source of phosphorus for the Mediterranean environment, the potential biological role of which depends on its solubility in rain and seawater. The atmospheric input of iron of Saharan origin is the main source of dissolved iron in the western Mediterranean.

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