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Impact of high Saharan dust inputs on dissolved iron concentrations in the Mediterranean Sea

C. Guieu,¹ Y. Bozec,^{2,3} S. Blain,² C. Ridame,¹ G. Sarthou,² and N. Leblond¹

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[1] During the PROSOPE cruise (Sept. 1999) in the Mediterranean Sea, dissolved iron concentrations in seawater and iron and aluminium concentrations in aerosols collected on board were investigated. Concentrations in aerosols were about two times higher in the Tyrrhenian Sea than in the west (Alboran Sea). This was in good agreement with the observed increase in dissolved iron concentrations in the surface waters from West to East. Depth profiles were characterised by a maximum in the surface mixed layer. Using an in vitro experiment, iron released from Saharan dust during the season characterized by a stratified water column and a low primary productivity was estimated: it resulted in an accumulation of 0.5–0.8 nM dissolved iron, in good agreement with the observed iron enrichment in the surface water (0.8 nM). This study confirms the significance of atmospheric input of Saharan origin on the iron cycle in the Mediterranean Sea. *INDEX TERMS:* 1065 Geochemistry: Trace elements (3670); 1050 Geochemistry: Marine geochemistry (4835, 4850); 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801). *Citation:* Guieu, C., Y. Bozec, S. Blain, C. Ridame, G. Sarthou, and N. Leblond, Impact of high Saharan dust inputs on dissolved iron concentrations in the Mediterranean Sea, *Geophys. Res. Lett.*, 29(19), 1911, doi:10.1029/2001GL014454, 2002.

1. Introduction

[2] The Mediterranean sea is strongly influenced by atmospheric inputs into the water column. This is due first to the close vicinity of the Saharan desert, which provides a source for considerable amounts of dust, and second to the strong stratification of the surface water column during a large part of the year which dramatically reduces exchange between surface and deep waters.

[3] Input of Saharan material represents approximately 90% of the total atmospheric particulate fallout to the water column [Loÿe-Pilot *et al.*, 1986] and is a major source of elements of biogeochemical importance such as iron (Fe). Indeed in the Western Mediterranean, Fe associated with Saharan dust represents 96% of the total atmospheric flux of Fe and Saharan dust is the main source of dissolved iron [Guieu *et al.*, 2002]. During the period of water column stratification in this area (June–October), the strong strat-

ification and the low surface production may allow atmospheric iron to accumulate in the surface mixed layer [Sarthou and Jeandel, 2001]. In contrast, after the spring bloom of phytoplankton, and in the absence of any Saharan dust input, the surface mixed layer can become Fe-depleted, with concentrations lower than 0.1 nM [Sarthou and Jeandel, 2001].

[4] The aim of this study was to investigate the effect of strong atmospheric inputs on the dissolved iron concentrations in the Mediterranean Sea.

2. Material and Methods

2.1. Water and Aerosol Sampling

[5] Samples were collected on board R/V *Thalassa* during the PROSOPE cruise (PROductivity of PELagic Oceanic Systems). The cruise took place from 4 September (Agadir, Morocco) to 4 October (Toulon, France) 1999. The cruise track can be seen in *Clauster et al.*, 2002.

2.1.1. Aerosols sampling

[6] Aerosol sampling was performed while the ship was underway while exhaust fumes were not blowing across the sampler to avoid any contamination. A small volume pump (Reciprotor AB, Sweden) was connected to a polycarbonate filter holder (Sartorius) installed at the front of the ship fourteen meters above sea level. Nuclepore filters (0.4- μ m pore diameter, 47 mm) were installed (removed) on (from) the filter holder inside the clean container. Collected air volume varying between 14 and 25 m³.

2.1.2. Water sampling

[7] Water samples were collected throughout the water column (0–2000 m) at two 5-day drifting stations (MIO, 33°58N, 22°00E and DYFAMED, 43°22N, 7°52E); surface samples were collected at two different depths (5 m and 10 m) at eight 4-hour stations. In the upper 200 m, a Teflon pump was connected to polyethylene tube attached to a Kevlar cable and used for sampling. In-line filtration (Nuclepore 0.4 μ m pore diameter, 47 mm) was performed in a laminar flow hood (class 100) in a clean laboratory container. Below 200 m, samples were taken from clean Niskin bottles and filtered immediately inside the clean container. The filtered samples were acidified on board to pH 2.0 with HNO₃ (Suprapur Merck) and stored in acid washed high-density polyethylene bottles.

2.2. Iron Analysis

2.2.1. Particulate iron and aluminium

[8] Aerosol samples were acid-digested inside a Milestone 1200 Mega microwave oven with 1 ml of HF and 3 ml of HNO₃ (Suprapur, Merck). Al and Fe were analysed in digested samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, 'Ultra Trace', Jobin Yvon) and concentrations determined using calibration

¹Laboratoire d'Océanographie de Villefranche-sur-Mer (LOV), CNRS, Villefranche-sur-Mer, France.

²Laboratoire des sciences de l'environnement marin (LEMAR), Institut Universitaire Européen de la mer, Plouzané France.

³Now at Netherlands Institute for Sea Research (NIOZ), Department of Marine Chemistry and Geology, Texel, The Netherlands.

Table 1. Elemental Concentrations in Aerosol Samples During the PROSOPE Cruise

Filter sample number	Collected between:	Fe $\mu\text{g m}^{-3}$	Al $\mu\text{g m}^{-3}$	Fe/Al $\mu\text{g}/\mu\text{g}$
AERO-5	St.1-St.2	0.14	0.36	0.4
AERO-6	St.2-St.3	0.44	0.75	0.6
AERO-7	St.3-St.4	0.24	0.44	0.6
AERO-8	St.4-St.5	0.14	0.28	0.5
AERO-9	St.5-St.6	0.21	0.14	1.5
AERO-10	St.6-St.7	0.13	0.19	0.7
AERO-11	St.7-St.8	1.07	1.94	0.6
AERO-12	St.8-St.9	0.35	0.54	0.6

Aerosol sampling was performed while the ship was underway between two stations.

graphs. Blanks (reagents alone and reagents + blank filter) were below the detection limit. Recovery obtained on a certified reference material (MESS, National Research Council of Canada) were: Al = $92\% \pm 3\%$ ($n = 6$); Fe = $101\% \pm 2\%$ ($n = 6$), indicating a good accuracy of the digestion/analysis.

2.2.2. Dissolved iron

[9] Dissolved iron was analysed according to a chemiluminescent method adapted from *Obata et al.* [1993] [see *Bucciarelli et al.*, 2001]. Calibration curves were performed using known iron additions in oceanic samples with low iron concentrations (that were below the detection limit). The detection limit (3 standard deviations of 10 replicates of blank) was 0.14 nM. Accuracy of the method was assessed using the international reference material: NASS-5 (North Atlantic Surface Seawater, National Research Council of Canada): 3.69 ± 0.62 nM certified value, 3.60 ± 0.04 nM determined.

2.3. Dissolution Experiment

[10] Saharan soil was used to perform the in vitro experiments in place of Saharan aerosols. This soil was representative of the Saharan aerosol transported over the Mediterranean. [*Guieu et al.*, 2002]. Various amounts of Saharan soil were introduced into ultra-pure water in order

to mimic dissolution processes occurring during a Saharan dust event. The experiment is fully described in *Ridame and Guieu*, [2002] and results are issued from *Ridame*, [2001].

3. Results

3.1. Iron Concentrations

3.1.1. Aerosols concentrations

[11] Aerosols concentrations ranged between 0.13–1.07 $\mu\text{g.m}^{-3}$ for iron and 0.14–1.94 $\mu\text{g.m}^{-3}$ for aluminum (Table 1). The highest concentrations were found in the central part of the western Mediterranean (between station 2 and 4) and during the transect between MIO and DYFAMED.

3.1.2. Dissolved iron

[12] Dissolved iron concentrations (Table 2) ranged from 0.26 to 2.72 nM in the upper 200 m. These concentrations are generally higher than concentrations in open ocean waters and are consistent with previously published values in the same area [*Sarthou and Jeandel*, 2001, and references therein]; In deep waters, concentrations varied between 0.13 and 1.08 nM and are typical of open ocean ones [*Johnson et al.*, 1997].

[13] The upper water column was strongly stratified with a surface mixed layer of 20–30 m. The vertical profiles of dissolved iron in the upper 150 m were quite similar at stations MIO and DYFAMED (Figure 1). Maximum surface concentrations of 1.75 ± 0.35 nM ($n = 2$) and 1.30 ± 0.10 nM ($n = 2$) were observed at stations MIO and DYFAMED, respectively. Below the thermocline, concentrations decreased rapidly and remained constant up to 150 m (0.42 ± 0.15 nM at MIO and 0.51 ± 0.10 nM at DYFAMED).

[14] Below 150 m, the dissolved iron concentration increased up to a maximum of 1nM (Figure 2). The depths of the iron maximum are different at both stations (200 m at MIO and around 400 m at DYFAMED), but are consistent with the depths of the maximum of salinity characterizing the Levantine Intermediate Water (LIW). At 2000 m, concentrations are equal to 0.33 and 0.52 nM at MIO and DYFAMED, respectively.

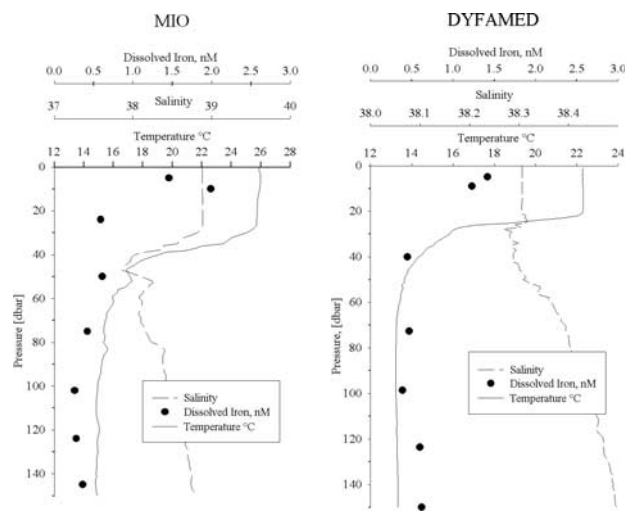
Table 2. Dissolved Iron Concentrations (nM) During the PROSOPE Campaign

Long occupation stations				Short occupation Stations		
'MIO'		'DYFAMED'				
depth	Fe	depth	Fe	site	depth	Fe
				2	5	1.17
5	1.46	5	1.42	2	10	0.70
10	1.99	9	1.23	3	5	1.09
24	0.59	20	3.1*	3	10	0.93
50	0.61	40	0.45	4	5	1.79
75	0.42	73	0.47	4	10	1.93
102	0.26	99	0.39	5	5	2.59
124	0.28	124	0.60	5	10	2.00
145	0.36	150	0.62	6	5	1.54
175	13.5*	173	0.51	6	10	2.00
188	1.08	193	0.57	7	5	1.77
200	0.78	200	3.5*	7	10	2.72
450	0.59	450	1.08	8	5	2.54
1000	0.13	1000	1.06	8	10	1.60
2000	0.33	2000	0.52	9	5	1.50
				9	10	2.70

Depth in dba.

The data labelled (*) are suspected to be contaminated.

Crosses denote the sampling mode used.

**Figure 1.** Depth profiles of temperature ($^{\circ}\text{C}$), salinity and dissolved iron (nM) in the upper 150 m at stations MIO (a) and DYFAMED (b).

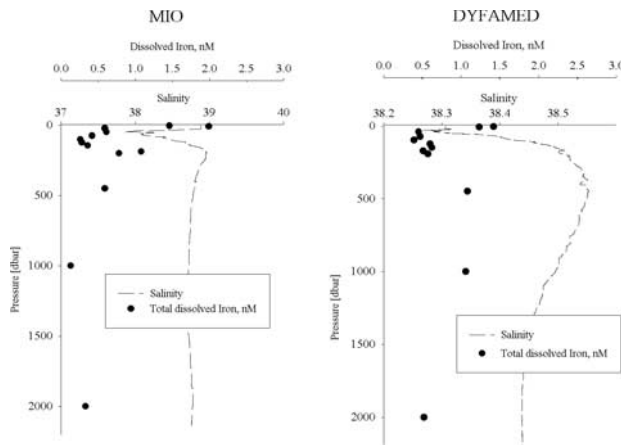


Figure 2. Depths profiles (0–2000 m) of salinity and dissolved iron (nM) at stations MIO(a) and DYFAMED (b).

[15] In the surface mixed layer, the highest dissolved iron concentrations ($\sim 2\text{--}2.5$ nM) were found at stations 5, 7, 8 and 9 located in the Tyrrhenian Sea and/or close to Sicily. The lowest concentrations (~ 1 nM) were found in the western Mediterranean (stations 2, 3). The average dissolved iron concentrations in the surface mixed layer gradually increased from west to east.

3.2. Dissolution Experiment

[16] The percentage of iron released in pure water by Saharan dust as a function of the amount of dust added is shown in Figure 3. The highest dissolution (0.24 %) was observed with the lowest amount of dust (5 mg l^{-1}). The percentage of iron released from the dust decreased for higher particulate loads following a logarithmic law.

[17] The experiment described above was conducted to mimic the dissolution process in rainwater and the logarithmic law can be applied knowing the amount of dust (mg l^{-1}) measured for a Saharan rain. For the events with no measurable rainfall (dust is deposited with only few drops of rainwater, the raindrops are evaporated immediately and all the dissolution will occur in seawater), the same dissolution law can be used, in a first approximation, to evaluate the amount of dissolved iron released from the particles in the water column. This approach is a first approximation as dissolution in ultra-pure water is not representative of dissolution processes that may occur in seawater. Indeed, the lower ionic strength of ultra-pure water and the absence of ligands may lead to an underestimation of the amount of dissolved iron released. On the other hand, the solubility of iron is related strongly to pH [Guieu and Thomas, 1996] and at pH 7 (pH resulting from Saharan dust addition in pure-water), Fe is more soluble than at seawater pH. Thus, this approach has to be considered as a rough estimate of the amount of dissolved iron released in seawater from these particular events that can not be considered as dry deposition.

4. Discussion

[18] During the campaign, sampled aerosols exhibited strong variations in Fe and Al concentrations. From direct observation onboard, and satellite imagery (not shown), as

the ship was traversing between stations 2 and 4, a Saharan dust plume was entering the Mediterranean atmosphere. Concentrations reported for the two corresponding samples (Table 1: AERO 6 and 7) exhibit an Fe/Al ratio very similar to the one determined for the Saharan end-member (0.63 ± 0.02 , Guieu *et al.*, 2002). Two additional samples are thought to reflect a Saharan origin (AERO 11 and 12): they were collected in the Tyrrhenian Sea and exhibit high concentrations in both Fe and Al, comparable to the values reported by Chester *et al.*, [1984] for Saharan aerosols collected in the same area. For these two samples, the Fe/Al ratio is also representative of the Saharan end-member. Indeed, for these samples, the three-dimensional, four-day air mass back trajectories calculated by Météo France at surface level (not shown) indicated a transport from the south-west close to the Libyan coastal area. Aerosol iron concentrations were about two times higher in the Tyrrhenian Sea than in the west (Alboran Sea). This may explain the increase in dissolved iron concentrations from West to East in the surface mixed layer.

[19] Dissolved iron depth profiles at stations MIO and DYFAMED indicate a significant enrichment in the surface waters. During the period of water column stratification, the surface mixed layer is isolated from deeper waters, and the atmosphere is the main source of nutrients such as iron and phosphorus to the surface waters [see for example, Ridame and Guieu, 2002]. The strong stratification and the low surface production should allow the atmospheric input of dissolved iron to accumulate in the mixed layer.

[20] At the DYFAMED station, the observed iron enrichment in the surface layer was equal to 0.8 nM [i.e., $1.3_{(\text{surface conc.})} - 0.5_{(\text{conc. below the thermocline})}$]. In an attempt to link this observed iron enrichment with the Saharan dust input in the central Ligurian Sea, we have calculated from the dissolution experiments, the dissolved iron concentrations which may result from the Saharan dust input measured at two coastal sites of the Ligurian Sea.

[21] In 1999, from June to the end of September (end of the PROSOPE cruise), a total dust flux of 2.4 t km^{-2} was recorded at Villefranche-sur-Mer [Ridame and Guieu, 2002] while a total dust flux of 5.9 t km^{-2} was recorded in Corsica (Loÿe-Pilot, pers. com). Considering that the Saharan dust is characterised by a total iron concentration of 4.5% [Guieu *et al.*, 2002], the Saharan source represented, from June to end

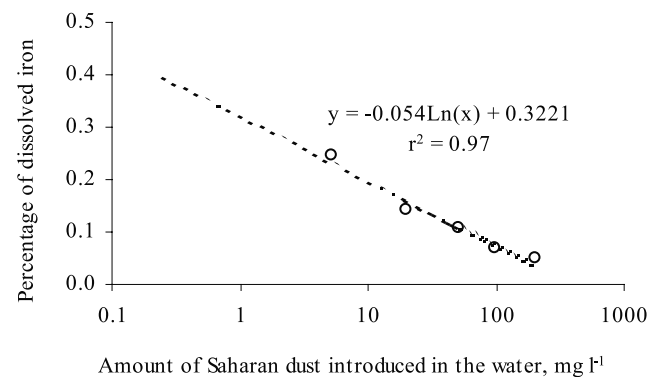


Figure 3. Percentage of dissolved iron vs. the quantity of Saharan dust (in mg l^{-1}) introduced in ultrapure water (see text for the experimental protocol).

of September, a total iron flux of $193 \times 10^4 - 475 \times 10^4$ nmol.m⁻². During the considered period, all dust deposition came with wet deposition with a high proportion of events with no measurable rainfall. The calculated (from the dissolution law) dissolution percentage in rains (with measurable rainfall) ranged from 0.05% to 0.3%. The total amount of dissolved iron released was then calculated by summing the estimated amounts of dissolved iron carried by individual events. For the events with no measurable rainfall, the dissolution in rainwater can be considered as negligible and the main dissolution process will occur in seawater [Ridame and Guieu, 2002]. Because more than 60 to ~90% of these particles have a median diameter below 1 μm [Chester and Johnson, 1971; Guieu et al., 2002], the residence time, of these particles, in the surface layer is long. Based on Stokes law, the sedimentation rate of the mineral particles in seawater can be computed as a function of particle size: a size-fraction lower than 1 μm settle at rates ≤ 5 cm day⁻¹ [Ridame and Guieu, 2002]. Consequently, these fine particles will accumulate in the surface layer during the entire stratified period while dissolution processes occur. The dust flux (mg m⁻²) actually measured for each of these events has been assumed to disperse over the upper 15–20 m surface layer; from the corresponding particle concentration in seawater (in mg l⁻¹), the percentage of dissolution was deduced from the logarithmic law (section 3.2). The obtained dissolution percentage ranged from 0.4 to 0.6%.

[22] These values are of the same order of magnitude as values reported in the literature [Jickells and Spokes, 2001 and references within] for crustal aerosol. It is one order of magnitude higher than the previous estimation of Guieu and Thomas [1996]. This discrepancy results from the larger grain size of the desert soil used by Guieu and Thomas [1996].

[23] The total dissolved concentration from atmospheric input that is predicted to accumulate in the surface mixed layer (15–20 m) was then calculated as the sum of the iron released in rainwater and in seawater: it varied between 0.5 and 0.8 nM.

[24] This calculation is an upper limit, as it assumes that the residence time of iron is longer than the oligotrophic period and because we consider negligible effects of phytoplankton uptake, scavenging and physical mixing in the surface mixed layer during this period.

[25] This estimation is in good agreement with the observed dissolved iron accumulation (0.8 nM) and supports the atmospheric origin from Sahara of the iron enrichment observed in the Mediterranean Surface Water.

[26] The other important feature of the iron profiles at DYFAMED and MIO stations is the deep iron maximum related to the occurrence of the LIW. The LIW results from sinking of Mediterranean Surface Water in the eastern part of the basin. The LIW flows back to the west at intermediate depths. The deep iron maximum may be the fingerprint of the surface origin of the water masses, which is consistent with the deepening of the maximum between MIO and DYFAMED.

[27] This study confirms the significance of the atmospheric input of dust of Saharan origin on the iron cycle in the Mediterranean Sea. Further investigations are currently in progress with regard to the impact of these inputs on the biological functioning of the Mediterranean Sea, in particular during the season characterized by a stratified water column and low primary productivity.

[28] **Acknowledgments.** The captain and the crew of the RV Thalassa and H. Claustre are gratefully acknowledged. The authors thank M.D. Loÿe-Pilot for data of Saharan flux measured in Corsica, D. Tailliez for providing the CTD data and M. Lewis for his help with the English. The helpful comments of the two anonymous reviewers are gratefully acknowledged.

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C. Guieu, C. Ridame, and N. Leblond, Laboratoire d'Océanographie de Villefranche-sur-Mer (LOV), CNRS, Villefranche-sur-Mer, France.

Y. Bozec, S. Blain, and G. Sarthou, Laboratoire des sciences de l'environnement marin (LEMAR), Institut Universitaire Européen de la mer, Plouzané, France.