

Atmospheric forcing on the annual iron cycle in the western Mediterranean Sea: A 1-year survey

Sophie Bonnet¹ and Cécile Guieu¹

Received 9 August 2005; revised 23 December 2005; accepted 30 March 2006; published 7 September 2006.

[1] A 1-year survey of simultaneous measurements of total atmospheric deposition and dissolved iron concentrations in surface waters (0–40 m) was performed in the northwestern Mediterranean Sea, an area with a marked seasonal hydrological regime. The total atmospheric iron flux was 1118 mg m^{-2} (i.e., 20.4 mmol m^{-2}). By using aluminium as a crustal marker the deposition was mainly attributed to Saharan dust deposition. Dissolved iron flux was estimated to be $42 \text{ } \mu\text{mol m}^{-2} \text{ yr}^{-1}$, of which 44% was anthropogenic in origin and 56% was of Saharan origin. Dissolved iron profiles revealed four typical situations throughout the year: (1) a winter situation with homogenous dissolved iron concentrations ranging from 0.8 to 0.9 nmol L^{-1} , (2) a spring situation with uniformly low concentrations ranging from 0.2 to 0.5 nmol L^{-1} , (3) a summer situation with enriched surface waters up to 1.2 nmol L^{-1} , and (4) an autumnal situation with homogenous concentrations ranging from 0.9 to 1.1 nmol L^{-1} . The results demonstrate that the iron enrichment in the mixed layer observed during the stratified period was of the same order of magnitude as the cumulative atmospheric inputs for the same period. The seasonal variability of dissolved iron (DFe) concentrations in surface waters was driven by a combination of factors, including aeolian Fe deposition, nature of aerosols, vertical mixing, phytoplankton uptake, and particle scavenging. Iron distribution can have a clear biogeochemical effect on the autotrophic communities: The low Fe:P ratio observed during the bloom indicates a possible iron limitation for phytoplankton, and the dissolved iron enrichment during summer is certainly at the origin of the development of diazotrophs populations in the system.

Citation: Bonnet, S., and C. Guieu (2006), Atmospheric forcing on the annual iron cycle in the western Mediterranean Sea: A 1-year survey, *J. Geophys. Res.*, *111*, C09010, doi:10.1029/2005JC003213.

1. Introduction

[2] Iron (Fe) is an essential micronutrient for phytoplankton growth. It is now recognized as a limiting factor for primary productivity in at least 40% of the oceans like “High Nutrient Low Chlorophyll” regions [Martin *et al.*, 1994; Coale *et al.*, 1996; Boyd *et al.*, 2000] but also in other large areas such as the North Atlantic [Blain *et al.*, 2004; Mills *et al.*, 2004] or Pacific resurgences [Bruland *et al.*, 2001; Hutchins *et al.*, 2002]. In ocean regions such as the subtropical gyres where fixed nitrogen supply is suggested to limit productivity, Fe also has a role in the stimulation of N_2 fixation [Michaels *et al.*, 1996; Karl *et al.*, 1997; Falkowski, 1997]. Since Fe has been recognized as a key element in ocean biogeochemical cycles, many studies have increased our understanding of the iron cycle in seawater. The abundance and availability of iron is controlled by a complex set of processes, including interactions with particulate matter and complexing organic molecules, biological utilization and export, and aeolian deposition of iron-rich

dust. Desert dust aerosols are indeed the dominant external input of iron to the open ocean [Jickells *et al.*, 2005]. Mineral aerosols consist of soil particles that are lifted into the atmosphere when strong winds occur over erodible surfaces. These Fe-rich particles can be transported over long distances from their source regions before deposition on the surface of the sea. The solubility of mineral and anthropogenic Fe is generally estimated to be only 0.05% to 14% of the total Fe, on the basis of a variety of laboratory experiments [Spokes and Jickells, 1996; Guieu *et al.*, 2002b; Bonnet and Guieu, 2004], with only a small fraction suspected to be available for the biota [Wu *et al.*, 2001]. Dust production, transport and deposition processes are highly spatially and temporally variable [Moulin *et al.*, 1997]. Desertic dust was recently reported to have significantly enhanced the surface dissolved iron (DFe) concentrations in some regions [see, e.g., Boyle *et al.*, 2005; Statham and Hart, 2005; Sarthou *et al.*, 2003; Johnson *et al.*, 2003; Guieu *et al.*, 2002b], but data on the seasonal variability of DFe in the open ocean in relation to the atmospheric flux remain sparse. We report here the first detailed study of a 1-year cycle of DFe distribution in the surface waters in relation to atmospheric inputs.

[3] The survey took place in the Mediterranean Sea, an oligotrophic, quasi-enclosed basin receiving the highest rate

¹Laboratoire d’Océanographie de Villefranche, Villefranche sur mer, France.

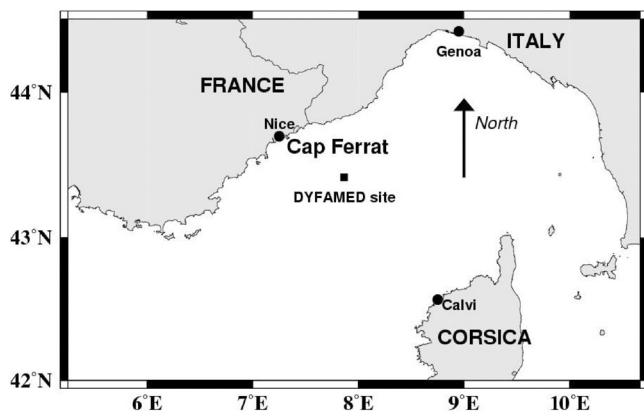


Figure 1. Location of the sampling sites: Atmospheric sampling at the Cap Ferrat signal station; seawater sampling at the DYFAMED site.

of aeolian material deposition in the global ocean [Guerzoni *et al.*, 1999]. In addition to these pulses of mineral dust, it continuously receives anthropogenic aerosols from industrial and domestic activities from populated areas around the basin and other parts of Europe that form a background over the Mediterranean Sea [Chester *et al.*, 1996; Guieu *et al.*, 1997]. This marine site is characterized by a strong thermal stratification in summer and fall, with a sharp pycnocline (10–20 m deep), associated with an efficient pycnocline acting as a physical barrier, where diffusion is extremely low (L. Prieur, personal communication, 2005). Moreover, horizontal advection has been shown to be weak at this site [Andersen and Prieur, 2000]. The upwelling of dissolved elements from depth is reduced during the stratified period, and the atmosphere becomes the main pathway of nutrient supply for the surface layer [Migon *et al.*, 2002; Ridame and Guieu, 2002]. These situations make the Mediterranean Sea an excellent natural laboratory to study the atmospheric control on the marine Fe cycle. Despite the occurrence of high atmospheric fluxes of Fe in this area, Sarthou and Jeandel [2001] reported a Fe-depleted (DFe $< 0.1 \text{ nmol L}^{-1}$) surface mixed layer (ML) at the end of the spring. This suggests that Fe can become a limiting factor for phytoplanktonic communities, including nitrogen fixers, during spring and summer seasons. The concomitant examination of DFe, biological activity, and atmospheric supply of Fe in the Mediterranean Sea has never been established, and we do not fully understand the mechanisms controlling Fe distribution in this area and thus its actual role in the functioning of this ecosystem. Here we present the first detailed assessment of the annual Fe cycle in an open ocean system.

[4] The objectives of this study were (1) to evaluate the magnitude and composition of the input of atmospherically transported material to sea surface and (2) to investigate DFe concentrations in surface seawater in order to better understand the biogeochemical functioning of the Mediterranean Sea. On the basis of this survey, conducted at the permanent time series DYFAMED station, we discuss the key processes controlling the supply and removal of DFe to and from the surface waters throughout the year and its biogeochemical implications on the ecosystem. For guid-

ance in interpreting the Fe data, hydrological and biological parameters obtained during the same period on each cruise are discussed.

2. Sampling and Methods

2.1. Atmospheric Sampling

[5] The total atmospheric deposition was collected at the Cap Ferrat site (altitude 138 m), a station located on a peninsula close to the town of Nice (Figure 1). This site is exposed to both natural and anthropogenic inputs [Chester *et al.*, 1996; Migon *et al.*, 2002].

[6] Total atmospheric deposition was collected continuously from January 2004 to February 2005 and 22 samples representing time periods of about 16 days were analyzed. The collector was made of a 4 L polyethylene bottle placed at 3 m from the ground. A polyethylene funnel was placed on the top of the bottle (surface 113 cm^2). A nylon mesh (porosity $20 \mu\text{m}$) covered the funnel in order to prevent insects and organic debris from falling inside the bottle. The 4 L bottles were filled with 200 mL of thymol solution (2.5 g L^{-1} , pH 6) to avoid bacterial development and minimize exchanges between the dissolved and particulate phases during the ~ 2 -week sampling (see section 2.3). After collection, the samples were carried back to the laboratory and were filtered through a $0.2 \mu\text{m}$ polycarbonate filter under a laminar flow hood (class 100). In order to collect all the particles stuck to the walls, a given volume of ultra pure water was then poured into the bottles and then ultrasonicated for 15 min. Large (local) debris were discarded from the funnel and the mesh. The funnel and mesh were then rinsed three times with ultrapure water with a clean glove. This water was then filtered in order to recover, as much as possible, the total amount of the particulate phase contained in each sample. The filters were then dried and weighed. After observation (binocular) and weighing, filters were acid digested inside a Milestone 1200 Mega microwave oven with 1 mL of Hexanoyloxyfucoxanthin (HF) and 3 mL HNO_3 ($^{\text{R}}$ Suprapur, Merck). Aluminium (Al) and Fe were determined using calibration curves by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES “Ultra traces,” Jobin Yvon). Blanks (reagent alone and reagent with blank filter after filtration of a thymol solution) were below the detection limit. Recovery obtained on two certified reference materials (MESS ($n = 3$) and BCSS ($n = 3$), National Research Council of Canada; range of weights: 16.9–21 mg) were Al = $98 \pm 1\%$ and $94 \pm 5\%$, Fe = $97 \pm 2\%$ and $101 \pm 1\%$, respectively, indicating a high accuracy of the digestion/analysis.

[7] All handlings were performed under ultra clean conditions to avoid any contamination. The material used for the experiment was initially prepared inside a clean room: It was first soaked in a surfactant bath for 1 week, then soaked for another week in a 50% HCl bath. Finally, it was ultrasonicated with HNO_3 ($^{\text{R}}$ Suprapur-Merck) for 5 hours and rinsed five times with ultrapure water.

2.2. Water Sampling

[8] Seawater was collected on board R/V *Téthys II* at the permanent time series DYFAMED site ($43^{\circ}25'N$, $07^{\circ}52'E$, 50 km off Nice, France; Figure 1). This open sea site (2350 m depth) is protected from coastal inputs by the

presence of the coastal Ligurian current. The survey took place from February 2004 through February 2005 with time periods of about 29 days. Seawater was collected every 5 m at nine different depths from the surface level to 40 m using a trace metal clean Teflon pump connected to a polyethylene tube. Inline filtration was performed through a 0.2 μm cartridge (Sartorius Sartobran-P-capsule 0.45 μm prefilter and 0.2 μm final filter) under a laminar flow hood (class 100). Samples were collected in triplicates into acid washed LDPE 60 mL bottles and acidified to pH 2 (^{18}O Ultrapur HCl, Merck) for at least 24 hours before analysis. In the frame of the monthly survey at the permanent time series DYFAMED site, CTD profiles (SBE9plus, Sea-Bird Electronics), pigments analysis and nutrients concentrations were also monitored on each cruise from the surface level to 200 m.

[9] DFe concentrations were measured by flow Injection Analysis with online preconcentration and chemiluminescence detection (FIA-CL) (adapted from *Obata et al.* [1993]). The pH of the acidified samples was adjusted to 5 using ^{18}O Ultrapur ammonia and a 3 times purified ammonium acetate buffer before loading on the 8 hydroxyquinoline (8 HQ) preconcentration column. Calibrations curves were made every day using additions of known amounts of DFe to seawater with poor DFe concentrations. Four different ranges of calibration curves were generated depending on the DFe concentrations of the samples. The purification of the luminol solution through a column of 8 HQ improved both the blank and the detection limit. Two types of blanks were considered: a “blank manifold” and a “reagent blank.” The blanks were determined each day. The contribution of the blank manifold to the analysis (estimated using different times of preconcentration and extrapolating the signal to a preconcentration time equal to zero) was under the detection limit. The contribution of HCL, NH_4OH and buffer additions to the analysis was determined by standard addition of each reagent in seawater with low DFe. This reagent blank varied between 22 and 44 pM with a mean value of 34 ± 1 pM ($n = 7$). The detection limit, equal to 3 times the standard deviation of the blank manifold, ranged from 5 to 20 pM with an average value of 13 ± 8 pM ($n = 7$). Each sample was analyzed in triplicate. When at least two of the three runs agreed within expected reproducibility (10%), the average of the two or three concordant runs was taken as a correct concentration. If the concentration obtained deviated too much from the profile continuum expectations and seemed to be contaminated (as samples were collected in triplicate), one of the other sampled bottles was then analyzed (in triplicate).

2.3. Calculations

[10] The magnitude of the air to sea fluxes of trace metals is dependant on the concentrations of the metals in the air, the partitioning of the metals between the different origins of the aerosols, and the process by which the metals are removed from the air column (i.e., by “dry” or “wet” deposition modes). In order to evaluate the atmospheric influence on the DFe stocks in the water column, the DFe flux originating from the atmosphere was calculated from our total atmospheric deposition data. The weight considered for the calculations has been corrected from potential dissolution processes in the bulk sample by using dissolu-

tion numbers established in artificial rainwater [*Guieu et al.*, 2002b]. This calculation took into account the anthropogenic versus terrigenous partitioning and the dry versus wet partitioning. Once this partitioning was established, we used dissolution numbers from dissolution experiments performed in artificial rainwater and natural seawater to estimate the actual DFe originating from the atmosphere. These previously published dissolution experiments were performed with anthropogenic and Saharan particles that have been shown to be representative of pollution and Saharan dust end-members [*Guieu et al.*, 2002b; *Bonnet and Guieu*, 2004]. Calculation of the increase of DFe due to atmospheric deposition depends on the mixed layer depth (MLD). The MLD is thus a key parameter for the entire computation. It was calculated following the same method used by *Levy et al.* [1998] where it is diagnosed as the depth at which density differs from surface density (5 m) by 0.05 kg m^{-3} . In order to take into account the uncertainties in the determination of this key parameter, we carefully considered a range value of $\text{MLD} \pm 30\%$. Our main objective was not to give exact values but rather an estimate based on a solid hypothesis and previously published data in order to evaluate the atmospheric influence on the DFe concentrations in surface waters.

2.3.1. Anthropogenic Versus Saharan Fe in the Total Atmospheric Deposition

[11] Each atmospheric sample collected for this study represents an integration of the total atmospheric fallout for a period of about 2 weeks. In these conditions, a single sample represents the mixing of fallout from air masses of different origins, with different loads of pollutants and natural aerosols. In the Mediterranean basin, desert dust coming from the Sahara represents the majority of the crustal fraction of atmospheric deposition [*Loye-Pilot and Martin*, 1996]. To identify the main source of Fe in each integrated sample, Al was used as a tracer of the Saharan particles. For the following calculation, we made the simple assumption that Fe has two main origins: crustal and anthropogenic. Aerosols coming from pyrogenic sources were shown to contribute to the Fe cycle at the regional scale [*Guieu et al.*, 2005], but during the sampling period (February 2004 to February 2005), burning biomass was particularly low compared to the average record: 100 km^{-2} were burned in the 15 departments of eastern southern France on the Mediterranean shore, which is half the mean annual surface recorded between 1973 and 2004 and 6 times lower than the surface burned in summer 2003 (<http://www.promethee.com/prom/upload/basedoc/15/bilan2004.pdf>). Thus we assume that the contribution of pyrogenic aerosol to the atmospheric input of Fe was negligible during the sampling period. The calculation of the percentage of non-Saharan Fe in each sample is reported in the caption of Table 1. The respective percentage of Fe of Saharan and anthropogenic origin in the total atmospheric deposition are reported in Table 1.

2.3.2. Dry Versus Wet Deposition

[12] Precipitation (mm) is recorded continuously by MétéoFrance at the Cap Ferrat signal station. Recorded precipitation was integrated over each sample's duration (Table 1). The partitioning between wet and dry deposition is crucial for the calculation of the DFe flux because Fe dissolution used for the calculation is different in rainwater

Table 1. Atmospheric Data Measured for Each Sampling Period at the Cap Ferrat Station^a

Dates	N	Rainfall, mm	MLD (Min-Max), m	Total Fe Flux, mg m ⁻² , mmol m ⁻²	Sources		Dry Versus Wet Partitioning				Resulting Dfe, nmol L ⁻¹ , in the MLD		
					Saharan, %	Anthropogenic, %	Saharan Dry, %	Anthropogenic, Wet, %	Saharan Wet, %	Anthropogenic Dry, %	Saharan Source	Anthropogenic Source	Total DFe MLD, nmol L ⁻¹
14 to 26 Feb 2004	1	29	290 (203–377)	988.3 (17.7)	100	0	0	100	-	-	5.93	0.020	0.020
11 Mar 2004	2	10	400 (280–520)	1.2 (0.02)	0	100	-	-	80	20	1.13	0.000	0.003
25 Mar 2004	3	0	258 (181–355)	3.6 (0.06)	46	54	100	0	100	0	8.34	0.029	0.032
8 Apr 2004	4	22	141 (99–183)	3.1* (0.05)	80*	20*	0*	100*	80	20	0.71	0.001	0.005
23 Apr 2004 ^b	5	25	28 (20–36)	2.6 (0.05)	96	4	0	100	80	20	0.28	0.006	0.010
14 May 2004 ^b	6	83	21 (15–27)	47.9 (0.86)	96	4	0	100	80	20	2.83	0.077	0.135
27 May 2004 ^b	7	0	14 (10–18)	0.2 (0.0)	0	100	100	0	100	0	0.08	0.000	0.006
15 Jun 2004 ^b	8	44	15 (10–18)	3.3 (0.06)	72	28	0	100	80	20	0.84	0.016	0.060
30 Jun 2004 ^b	9	0.6	16 (10–18)	0.8 (0.01)	0	100	100	0	-	-	0.22	0.000	0.016
15 Jul 2004 ^b	10	9	16 (11–21)	34.5 (0.62)	97	3	0	100	80	20	1.19	0.032	0.074
29 Jul 2004 ^b	11	3	17 (11–21)	2.5 (0.04)	65	35	100	0	100	0	1.74	0.093	0.109
17 Aug 2004 ^b	12	10	14 (10–18)	6.4 (0.11)	89	11	0	100	80	20	0.67	0.014	0.048
2 Sep 2004 ^b	13	1	15 (10–18)	3.3 (0.06)	76	24	100	0	100	0	1.89	0.119	0.135
22 Sep 2004 ^b	14	0	20 (14–26)	8.6 (0.15)	71	29	100	0	100	0	3.57	0.150	0.178
15 Oct 2004 ^b	15	23	36 (25–47)	7.2 (0.13)	98	2	0	100	80	20	0.44	0.002	0.006
2 Nov 2004 ^b	16	93	37 (26–48)	12.7 (0.23)	91	9	0	100	0	100	3.23	0.009	0.067
16 Nov 2004 ^b	17	17	38 (27–49)	2.1 (0.04)	0	100	-	-	80	20	1.41	0.000	0.037
30 Nov 2004	18	76	38 (27–49)	1.9 (0.03)	0	100	0	100	80	20	1.29	0.000	0.035
15 Dec 2004	19	17	50 (35–65)	3.8 (0.07)	76	24	0	100	80	20	0.85	0.003	0.017
21 Jan 2005	20	68	212 (148–276)	1.7 (0.03)	0	100	-	-	80	20	1.41	0.000	0.007
4 Feb 2005	21	13	729 (510–948)	1.9 (0.03)	0	100	-	-	80	20	1.82	0.000	0.002
5 to 22 Feb 2005	22	17	729 (510–948)	2.1 (0.04)	0	100	-	-	80	20	1.99	0.000	0.003
Cumul stratified period		309		131.6 (2.36)							18.39		
Annual Flux		561		1118 (20.42)							41.86		

^aAll the parameters used for the calculation of the resulting DFe in the ML are indicated in the table. The percentage of non-Saharan Fe in each sample (Xs) was calculated using the following formula: $Xs = 100/Fe_{sample} \times (Fe_{sample} - (Al_{sample} \times (Fe/Al)_{Saharan\ end-member}))$, with $(Fe/Al)_{Saharan\ end-member} = 0.63 \pm 0.02$ (from 10 Saharan rain events selected to be representative of Saharan inputs to the western Mediterranean Sea [Güieu *et al.*, 2002a]). Some of the samples had no rain, or extremely little rainfall (<3 mm), and were classified as “dry” samples. Over the period, six samples were “dry” (samples 3, 7, 9, 11, 13, and 14), and for those samples, the dissolution of Fe was assumed to take place in the surface seawater for both anthropogenic and Saharan aerosols. Two samples were classified as “wet” (samples 1 and 16) because they corresponded to a mostly rainy period, and for those samples, the dissolution of Fe was assumed to have taken place in the rainwater for both anthropogenic and Saharan aerosols. The remainder of the series was a combination of wet and dry deposition. Among these samples, those with aerosols mainly from Sahara were associated with rain events, and the percentage of Saharan origin computed according to the formula given above was attributed to wet deposition. For these “Saharan wet” samples, we considered that the main dissolution of Fe occurred in rainwater. For the anthropogenic fraction we used the mean proportion (80% dry, 20% wet) established from an atmospheric survey representing 45 rain events and collection of total atmospheric deposition for a period of 455 days in the northwestern Mediterranean Sea [Güieu *et al.*, 1997]. Given the rainfall and the total Fe concentration for each sample, the DFe from wet deposition associated with Saharan and anthropogenic particles was calculated in the volume of precipitations actually collected and extrapolated to the surface ML using the following calculation: $ADFe_{ML} (nmol\ L^{-1}) = ((\Delta DFe_{rain} (nmol\ L^{-1}) \times rain\ volume_{(L)}) / (MLD_{(m)} \times 1000)) / (MLD_{(m)} \times 1000)$, with $ADFe_{rain} (nmol\ L^{-1})$ deduced from dissolution experiments and Total Fe concentration_{rain} (nmol L⁻¹); 0.011 m² is the surface of the collector; MLD is the mixed layer depth. The total atmospheric Fe flux associated to dry deposition was directly converted to DFe in the surface ML using the following calculation: $ADFe_{ML} (nmol\ L^{-1}) = \%_{dissolution} \times (Total\ Fe\ flux_{(ng\ m^{-2})} / (MLD_{(m)} \times 1000) / 55.85)_{(g\ mol^{-1})}$.

^bSamples collected during the stratified period.

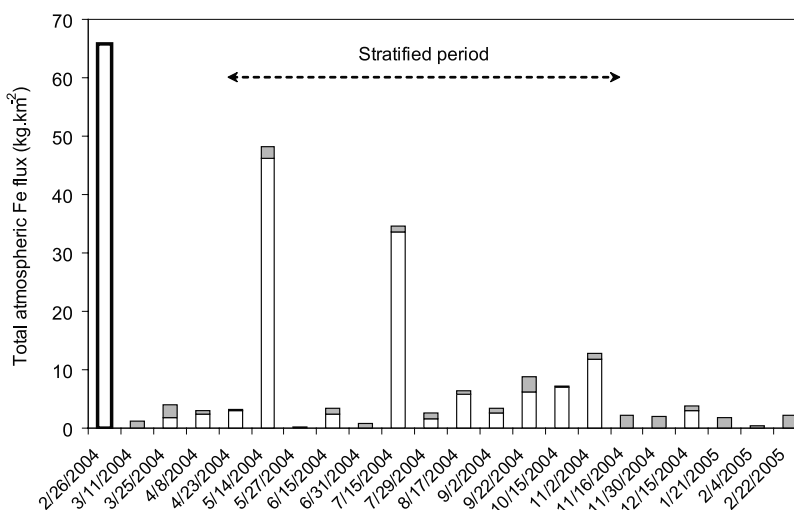


Figure 2. Temporal evolution of total atmospheric Fe fluxes (kg km^{-2}) for each ~two-week sample collected at Cap Ferrat station through the year studied. Shading in the histograms indicates the partitioning between (white) crustal fraction and (gray) anthropogenic fraction of the Fe flux. For the first histogram (sample 1, 14–26 February 2004) the flux was divided by 15.

(wet deposition) and seawater (dry deposition). Details on how this calculation was performed are given in the caption of Table 1.

2.3.3. Dissolved Versus Particulate Atmospheric Fe Flux

[13] The design of the sampling did not allow measurement of the distribution between the dissolved and particulate phases. Instead, the atmospheric DFe was estimated by using previously established relations that link iron dissolution to particulate mass in seawater and rainwater.

[14] For the wet deposition, after the mass flux was divided into a Saharan and an anthropogenic fraction, the DFe coming from the crustal fraction was calculated following the relation existing between the percentage of dissolution and the particulate mass for experiments conducted in ultrapure water (about pH 5.5) [Guieu *et al.*, 2002b]. The pH of the rain collected in the Mediterranean Sea has been reported to vary between 4 and 6 [Loye-Pilot and Morelli, 1988]. For the anthropogenic fraction, several studies have reported that Fe solubility in rainwater averages 14% [Schutysse *et al.*, 1978; Colin *et al.*, 1990; Guieu *et al.*, 1997]. More precisely, Guieu *et al.* [1997] reported that 12% of Fe is found in dissolved form in rain collected on a coastal site of the Mediterranean Sea. This later percentage was chosen for our calculations (details are given in the caption of Table 1).

[15] For the dry deposition, after the mass flux was divided into a crustal and an anthropogenic fraction, DFe was calculated following the relation existing between the percentage of dissolution and the particulate mass, for experiments conducted in seawater with anthropogenic particles and Saharan dust [Bonnet and Guieu, 2004]. The dissolution experiment conducted by Bonnet and Guieu [2004] was made using a fine fraction ($<20 \mu\text{m}$) of Saharan soils collected in the source region of Saharan aerosols. It was shown to be representative of the Saharan aerosols transported over the Mediterranean [Guieu *et al.*, 2002a]

and is considered the most appropriate reference for this study. Calculations are given in the caption of Table 1.

3. Results

3.1. Atmospheric Fluxes

3.1.1. Total Fe Flux

[16] Figure 2 shows the temporal evolution of total atmospheric Fe fluxes for each ~two-week sample through the year studied and the partitioning between crustal versus anthropogenic Fe flux. The total annual Fe flux (February 2004–February 2005) was 1118 kg km^{-2} (20.4 mmol m^{-2}). The data indicate a strong heterogeneity throughout the year with one extremely strong Saharan event on 26 February 2004, accounting for 88% of the total annual Fe flux. There were also two other Saharan events responsible for high Fe fluxes between 23 April and 14 May 2004, and between 30 June and 15 July 2004, accounting for 4% and 3%, respectively, of the total annual flux. An additional important Fe flux mainly attributed to Saharan input was recorded for the period between 15 October and 2 November 2004 and accounted for 1% of the total annual Fe flux. All other fluxes recorded were extremely low ($<0.6 \text{ kg km}^{-2} \text{ d}^{-1}$). When considering the entire series, over 99% of the total annual flux was attributed to a Saharan origin by way of a few strong pulses. The annual flux of Saharan dust recorded was 25 t km^{-2} compared to 0.6 t km^{-2} for anthropogenic particles.

3.1.2. Dissolved Fe Flux

[17] Table 1 indicates, for each atmospheric sample, the corresponding DFe flux ($\mu\text{mol m}^{-2}$), the resulting atmospheric DFe concentration in the surface ML (nmol L^{-1}), and the parameters used for this calculation. The DFe flux calculated for the entire period was $42 \mu\text{mol m}^{-2}$. The input of atmospheric DFe in the ML varied from 0.002 to $0.178 \text{ nmol L}^{-1}$, and the cumulative input of atmospheric DFe over 1 year in the ML was 1.01 nmol L^{-1} . This input was driven in large part by Saharan deposition (0.57 nmol

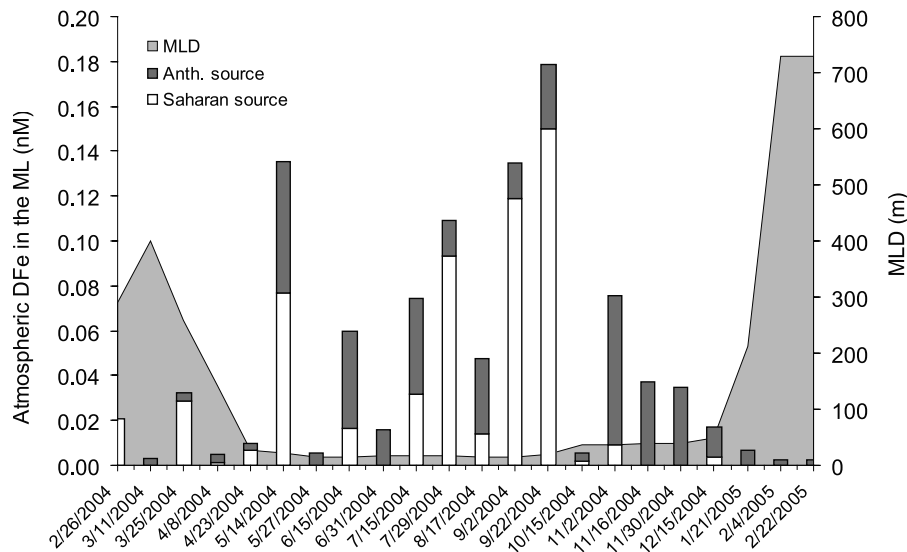


Figure 3. Atmospheric DFe entering the ML for each period of 2 weeks corresponding to atmospheric samples.

L^{-1}) and, less importantly, by anthropogenic deposition (0.44 nmol L^{-1}). Because MLD is minimum between May and October, atmospheric DFe entering the surface ML is maximum during that period (see Figure 3).

3.2. Hydrological and Biological Characteristics of the Study Site

[18] The permanent time series DYFAMED site has been studied monthly since 1991 (<http://www.obs-vlfr.fr/sodyf/home.htm>). This site is characterized by strong seasonal variations in both hydrological and biological parameters [Marty *et al.*, 2002]. The seasonal hydrological regime varies from strong thermal stratification in summer and fall to vertical mixing during winter. This maximal winter mixing occurs generally in February, and nutrients are then introduced into the surface layer. In 2004, the stratification of the water column began at the end of April 2004 and ended in November 2004 (Table 1).

[19] TChl *a* was at its peak (up to 1.2 mg m^{-3} on average on the 0–40 m upper layer) during the spring bloom in April 2004 and was dominated by large cells (microphytoplankton and nanophytoplankton) (Figure 4). Later in the year, the peak of biomass became less pronounced and descended to the deeper layers (30–50 m) following the nutricline during the summer and fall. At that period small cells represented the most part of the Chl *a* biomass in the surface layer. In 2004, the evolution of the hydrological and biological characteristics conformed to the average picture described in Marty *et al.* [2002].

3.3. Sea Surface Dissolved Fe Concentrations

[20] During the entire year, DFe concentrations in the surface layer (0–40 m) ranged from values of 0.19 to 1.22 nmol L^{-1} (Figure 5). This range is coherent with previously measured DFe concentrations at DYFAMED in September 1999 [GuiEU *et al.*, 2002b]. Vertical distribution of DFe concentrations showed a strong seasonal variation with homogenous concentrations during the winter season and very heterogeneous concentrations during the stratified period.

[21] In February 2004, concentrations were homogenous throughout the 0–40 m water column, and the average value was $0.81 \pm 0.07 \text{ nmol L}^{-1}$ ($n = 9$). In March, April, and May, the DFe concentrations were still vertically homogenous but much lower than in February ($0.49 \pm 0.04 \text{ nmol L}^{-1}$, $0.19 \pm 0.03 \text{ nmol L}^{-1}$ and $0.30 \pm 0.09 \text{ nmol L}^{-1}$, respectively ($n = 9$ for each)). During the stratified period (April to September), profiles were characterized by increasing subsurface DFe concentrations reaching $1.23 \pm 0.11 \text{ nmol L}^{-1}$ at the end of September. For technical reasons, we do not have values from the surface level to 15 m of depth in September 2004. For meteorological reasons, no cruise took place in October 2004, and we do not have a DFe vertical profile for this date.

[22] When the water masses began to mix in November, the DFe concentrations became vertically homogenous ($1.04 \pm 0.07 \text{ nmol L}^{-1}$, $n = 9$) and remained similar in December ($1.08 \pm 0.05 \text{ nmol L}^{-1}$). DFe concentrations decreased to 0.83 nmol L^{-1} in January and February 2005.

[23] Finally, we can highlight four typical situations throughout the year: (1) a winter situation with homogenous DFe concentrations ranging from 0.8 to 0.9 nmol L^{-1} , (2) a spring situation with uniformly low concentrations ranging from 0.2 to 0.5 nmol L^{-1} , (3) a summer situation with enriched surface waters up to 1.2 nmol L^{-1} , and (4) an autumnal situation with homogenous concentrations from 0.9 to 1.1 nmol L^{-1} .

4. Discussion

4.1. Atmospheric Deposition Over the Annual Cycle

[24] The total atmospheric deposition did not exhibit a strong seasonal imprint over the year studied. Loyer-Pilot and Martin [1996] showed that from an 11-year record of atmospheric input in Corsica, the frequency and the magnitude of the Saharan events achieve their maximum in spring and autumn and their minimum in winter, though with a high interannual variability. In our data set the highest dust flux was recorded during the winter season

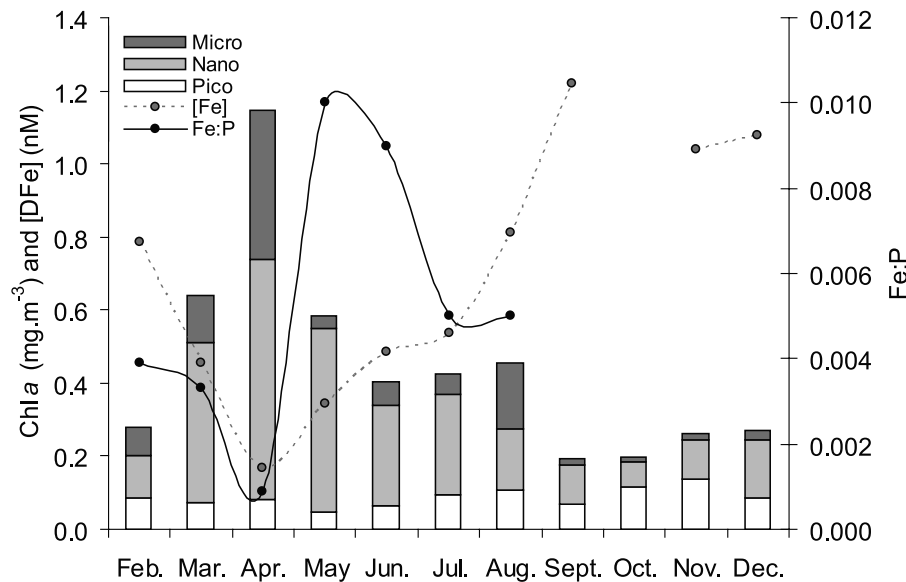


Figure 4. Chlorophyll *a* concentrations (mean concentrations over the 0–40 m upper layer: The sampling was performed on the rosette), divided into three size classes (picophytoplankton, nanophytoplankton, and microphytoplankton). The Fe:P ratio and the mean DFe concentrations in the 0–20 upper layer are superimposed. The biomass proportions of TChl *a* associated with picophytoplankton (<2 μm) (biomass proportion (BP) pico), nanophytoplankton (2–20 μm) (BPnano), and microphytoplankton (20–200 μm) (BPmicro) were calculated as described by Vidussi *et al.* [2001]: $\text{BPpico} = (\text{zea} + \text{TChl } b) / \text{DP}$, where DP is the sum of diagnostic pigments ($\text{DP} = \text{zea} + \text{TChl } b + \text{allo} + 19'$ Hexanoyloxyfucoxanthin (HF) + $19'$ Butanoyloxyfucoxanthin (BF) + fuco + peri), $\text{BPnano} = (\text{allo} + 19'\text{HF} + 19'\text{BF}) / \text{DP}$ and $\text{BPmicro} = (\text{Fuco} + \text{Peri}) / \text{DP}$.

(26 February) and accounted for 88% of the total annual Fe flux and 89% of the total Saharan dust flux. These types of high-magnitude and low-frequency events are responsible for the high interannual variability of the seasonal trend.

[25] The annual input of Saharan dust recorded in this study was 25 t km^{-2} , which is close to the highest that was recorded in this area between 1984 and 1994 by Loyer-Pilot and Martin [1996] (26.2 t km^{-2} in 1987). In addition to the input of anthropogenic particles, this total deposition corresponded to an annual total Fe flux of 1118 kg km^{-2} (20.4 mmol m^{-2}), which is of the same order of magnitude as that reported by Guieu *et al.* [1997] for 1988–1989–1990 ($945\text{--}851 \text{ kg km}^{-2} \text{ yr}^{-1}$) and 8 times higher than the mean annual Fe flux recorded by Ridame *et al.* [1999] in 1996 and 1997 in Corsica. The annual DFe flux estimated here ($42 \mu\text{mol m}^{-2}$) was 2 to 4 times lower than that recorded by Guieu *et al.* [1997] ($90\text{--}180 \mu\text{mol m}^{-2}$).

[26] The input of atmospheric DFe to the ML was maximum during the stratified period. This result suggests that the intensity of aeolian deposition is not the only factor controlling the DFe distribution in the surface ML. The other factor that drives the DFe atmospheric flux in surface waters is the MLD. During the stratified period, the reduced MLD (mean 20 m) acts as an almost “closed” reservoir; the surface waters are isolated from deeper ones by the physical barrier generated by the thermocline, and the atmosphere becomes the main pathway of Fe supply for the surface waters. As an example, the atmospheric Fe flux recorded during the first 2 weeks of July (sample 6: MLD: 21 m) accounted for 4% of the total annual flux but corresponded to more than 13% of the total annual DFe ($+0.135 \text{ nmol L}^{-1}$)

input to the water column. By contrast, the large Saharan event of February (sample 1: MLD: 290 m), which accounted for 88% of the total annual atmospheric Fe flux, corresponded to only 2% of the total annual atmospheric DFe input ($+0.02 \text{ nmol L}^{-1}$).

4.2. Atmospheric Imprint on Fe Marine Cycle

4.2.1. Stratified Period

[27] Our time series data quantifies for the first time the atmospheric forcing on DFe cycle in the water column of an oligotrophic region. In an attempt to link this observed DFe enrichment in the surface waters (average concentration in the surface ML: average concentration below the thermocline) with atmospheric inputs, the total amount of DFe released by the atmospheric inputs was calculated by summing the estimated amounts of DFe carried by individual event for each of the 6 months (May to October) of the stratified period (Table 1). The observed DFe enrichment in the surface waters along with the atmospheric inputs of DFe (with a distinction between Saharan and anthropogenic sources) are represented in Figure 6. Following the calculation methods described in the section Method/Calculations, the DFe concentration from atmospheric inputs that is predicted to accumulate in the ML varied from a range of $0.12\text{--}0.22$ in May to $0.64\text{--}0.98 \text{ nmol L}^{-1}$ in October. This is of the same order of magnitude as the observed DFe enrichment in the water column for the same period (0.13 in May to $\geq 0.88 \text{ nmol L}^{-1}$ in October) (Figure 6). It is quite surprising that the atmospheric input of DFe continuously accumulated during the stratified period, with no significant loss from the ML, to reach a level that was very close to the

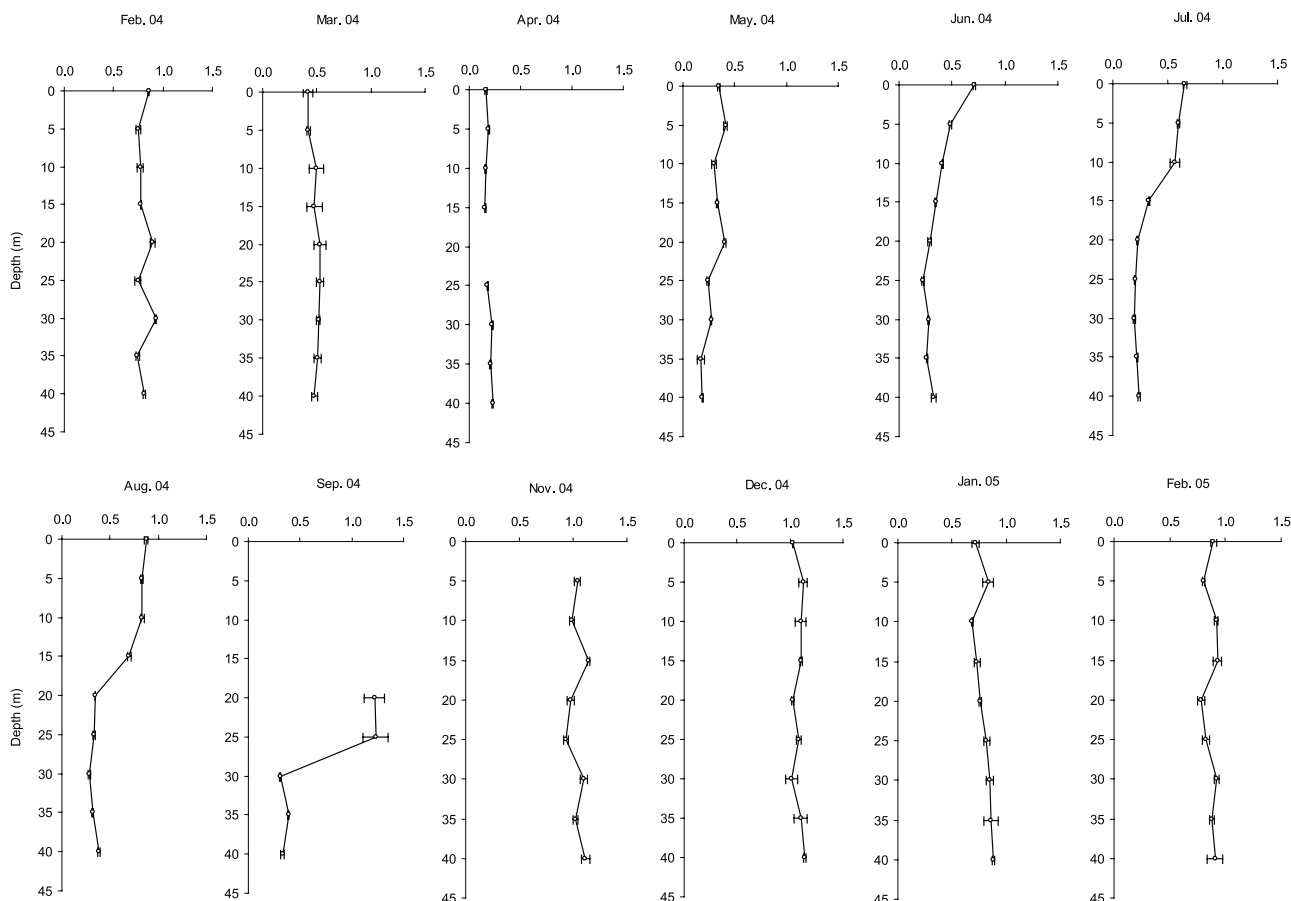


Figure 5. DFe profiles (nmol L^{-1}) in the upper 40 m at station Dyfamed.

actual enrichment observed in the surface ML in October. This would mean that recognized Fe-depleting processes such as phytoplankton uptake/adsorption, scavenging by particles and diffusion through the thermocline were negligible during this period.

[28] Phytoplankton uptake of Fe can be roughly estimated by using $\text{Fe/C} = 10^{-5} \text{ mol mol}^{-1}$ [Johnson *et al.*, 1997]: An average of 0.05 nmol L^{-1} DFe uptake in the ML for the integrated period May–July (no C data available after this date) indicates that the removal of DFe by this biological process was actually negligible compared to the in situ DFe. The largest sink for DFe in seawater after uptake by plankton was the scavenging of Fe by particles (biotic or abiotic). Clay minerals (aluminosilicates) and oxides present at the surface of the anthropogenic particles are known to have good adsorptive properties [de Baar and de Jong, 2001]. In fact, scavenging by mineral/anthropogenic particles has been taken into account in the dissolution numbers used to calculate the DFe input to the water column and are thus included in our calculation of DFe atmospheric flux. Bonnet and Guieu [2004] attributed the low dissolution of Fe associated with Saharan dust and anthropogenic particles observed in an abiotic experiment (0.05 to 2.2%) to the intense scavenging of DFe by mineral/anthropogenic particles. The same experiment performed on natural seawater (containing the natural assemblage) collected at DYFAMED in the summer of 2003 [Bonnet *et al.*, 2005] indicated the same dissolution percentages of Fe from Saharan dust compared to those obtained from the abiotic

experiment with the same dust concentration: We conclude that adsorption onto algae's surface (as described in Sigg [1998]) was negligible during low chlorophyll-stratified period. Export via adsorption onto biogenic particles such

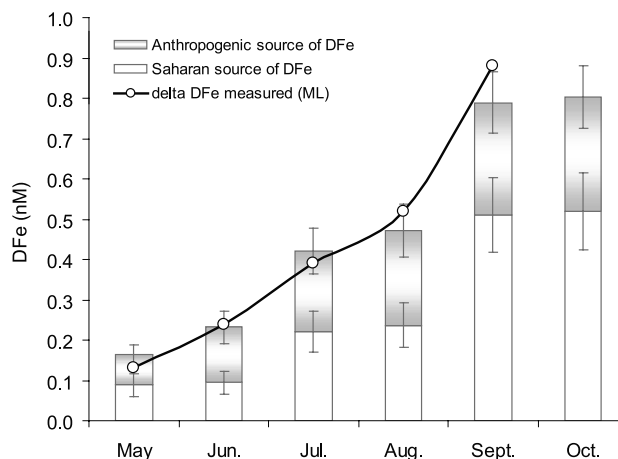


Figure 6. (black line) DFe enrichment measured in the ML (average concentration in the surface mixed layer: average concentration below the thermocline), and (histograms) total atmospheric DFe concentrations that were predicted from the calculations to accumulate in the ML for each month of the stratified period; the histograms show cumulative inputs from (grey) anthropogenic deposition and (white) Saharan dust.

as fecal pellets was not taken into account. Even if such particle flux was known to be quite low during the stratified period at the DYFAMED site [Stemann *et al.*, 2002], it should have participated in a withdrawal of a fraction of DFe, which we were unable to quantify. The loss of DFe from diffusion across the thermocline has also been calculated using an average diffusion coefficient of $0.3 \text{ cm}^2 \text{ s}^{-1}$ (L. Prieur, personal communication, 2005). This flux is very small and negligible ($1.4 \text{ nmol m}^{-2} \text{ d}^{-1}$) compared to the atmospheric flux of DFe ($\sim 100 \text{ nmol m}^{-2} \text{ d}^{-1}$).

[29] On the other hand, it should be noted that our atmospheric flux of DFe may possibly have been underestimated for two reasons:

[30] 1. Saharan rains can be associated with anthropogenic particles, and the resulting pH can be lower than that expected for a pure Saharan event; this leads to a possibly higher dissolution of Saharan Fe than that predicted by the percentages used (and thus a higher atmospheric DFe flux). For example, an increase of 100% of the dissolution of Fe attached to Saharan particles in “mixed” events would increase the total atmospheric DFe at the end of the stratified period by 0.03 nmol L^{-1} (3% of the total atmospheric DFe that enters the ML).

[31] 2. From aerodynamic considerations, the dry deposition could be underestimated by the type of collector used for the study [Ridame *et al.*, 1999]. The maximum underestimation based on comparison between rainfall measured by MétéoFrance gauge and our collector for the event where highest winds were observed is of 13%. If we apply this maximum value to all our numbers, it increases atmospheric DFe at the end of the stratified period by 0.06 nmol L^{-1} (7% of the total atmospheric DFe that enters the ML). Our conclusions on the temporal trends are therefore valid in spite of a possible slight underestimation (10% maximum) of the total DFe fluxes reported.

[32] A rough estimate of the residence time of DFe in the surface ML can be made by assuming that the major Fe source was aeolian and that the system was at steady state. Residence time was obtained by dividing the ML inventory of DFe accumulated during the stratified period (calculated from data shown in Figure 5) by the atmospheric flux of DFe from atmospheric particles occurring during the stratified period. This residence time was 5 months, which is long enough to observe a DFe accumulation during the stratified period. This residence time is lower than that calculated by Statham and Hart [2005] (0.7 to 2.0 years in the eastern Mediterranean Sea) but higher than that found in the upper 100 m of the north and equatorial Atlantic Ocean (1–2 months, de Baar and de Jong [2001]) where hydrodynamical conditions are completely different than those encountered in the Mediterranean environment.

[33] Our results demonstrate that the DFe enrichment in surface waters increased from May to October, indicating an accumulation of DFe ($\geq 0.88 \text{ nmol L}^{-1}$) of atmospheric origin in the ML throughout the summer. The strong stratification and the low biological activity may have allowed the atmospheric input of DFe to accumulate in the ML. These results are consistent with previous DFe profiles established by Guieu *et al.* [2002b], who reported an accumulation of 0.8 nmol L^{-1} in September 1999 at the DYFAMED site that was in strong agreement with the cumulated DFe flux originating from the Saharan events

that took place during the stratified period. These surface-enriched and subsurface-depleted DFe profiles also have a similar shape to those observed by Statham and Hart [2005] in the eastern Mediterranean Sea and Boyle *et al.* [2005] in early spring at ALOHA station, whose surface enrichments were attributed to Saharan and Asian dust deposition, respectively. However, the DFe accumulation on the ML found in our study was 3.5 times lower than the enrichment measured in October 1994 by Sarthou and Jeandel [2001] ($+3.1 \text{ nmol L}^{-1}$). This difference must be due to the different magnitude of atmospheric deposition between the 2 years, but above all, to their distribution over the year. The annual dust flux recorded in 1994 (4 t km^{-2}) [Loye-Pilot and Martin, 1996] was slightly higher than the flux recorded in 2004 (3 t km^{-2} without taking into account the large event of February 2004). We do not have any information concerning the distribution of these inputs in 1994, but it is possible that the majority of the dust deposition occurred during the summer season, explaining the high DFe measured at the end of the stratified period. This result suggests that DFe accumulation at the end of the stratified period must be variable according to the year considered; dust production, transport, and deposition processes are indeed temporally variable, which seems to result in various amounts of DFe accumulation at the end of the stratified period, depending on the annual Fe flux and on the repartitioning of it along the year.

4.2.2. Mixing Period

[34] During the mixing period, the DFe concentrations were homogenous in the upper 40 m with a highly variable mean concentration over the period. The DFe concentrations were about 0.9 to 1.1 nmol L^{-1} in November and December 2004. This period corresponded to the beginning of the mixing period; the MLD is about 50 m in depth and may indicate a mixing of the summer-enriched surface waters with poorer underlying water masses. Before the winter mixing, the water column had a homogenous 25 m ML whose DFe concentration was 1.22 nmol L^{-1} . Assuming that the DFe concentration in the layer 25–50 m is $\sim 0.5 \text{ nmol L}^{-1}$ [Guieu *et al.*, 2002b], a mixing from the sea surface to a depth of 50 m will result in a mixed autumnal DFe concentration of 0.9 nmol L^{-1} in the homogenized 50 m water column. This calculated value is of the same order of magnitude as the one observed (1 nmol L^{-1}). In January and February 2005, the DFe concentrations were lower than those of the previous 2 months (0.7 to 0.9 nmol L^{-1}). The corresponding MLD for these 2 months were 212 m and more than 700 m, indicating a dilution of the 50 upper meters with deep waters masses. Guieu *et al.* [2002b] have reported DFe concentrations of 0.55 nmol L^{-1} in the layer 50–200 m and of 1 nmol L^{-1} between 200 and 1000 m (this deep maxima being attributed to the presence of the Ligurian intermediate waters resulting from the sinking of Fe-rich Mediterranean surface water in the eastern part of the basin). From a simple calculation, a mixing from the sea surface to a depth of 700 m will result in a mixed wintertime DFe concentration of 0.83 nmol L^{-1} in the homogenized 700 m water column, which is very close to the DFe measured in January and February (0.79 and 0.87 nmol L^{-1} , respectively).

[35] March, April, and May correspond to the blooming period, and phytoplankton uptake contributed for a part to the Fe minimum values found in the first 40 m at that period. The theoretical amount of Fe taken up by phytoplankton (calculated as in previous section) was at its peak in April with a mean value of $0.15 \pm 0.03 \text{ nmol L}^{-1}$ over the 40 m water column and coincided with the lowest concentrations of DFe measured at that time in the water column. In contrast, the rate of scavenging by particulate matter is dependant both on DFe concentration and abundance of particles [de Baar and de Jong, 2001]. Even if a large part of scavenging processes by nonbiological particles were taken into account in the dissolution numbers used for this study, the higher abundance of particles during the blooming period at the DYFAMED site [Steemann *et al.*, 2002] suggests that intense scavenging by biological particles may have thus contributed to Fe export toward deeper waters. Moreover, phytoplanktonic and bacterial exudates may have enriched the pool of transparent exopolymeric particles (particles formed abiotically by coagulation of colloidal organic matter and substances exuded by phytoplankton and bacteria) in the water column. These particles (1 to 100 μm) also have a large complexing capacity of DFe due to their richness of anionic polysaccharides. Beauvais [2003] showed that these particles can adsorb up to 20 nmol of Fe in natural conditions per liter of coastal water.

[36] Sarthou and Jeandel [2001] have also reported surface DFe minima ($<0.13 \text{ nmol L}^{-1}$) in May, with a nutrient-like profile, similar to those reported in other oceanic basins. The phytoplanktonic bloom could have removed Fe very rapidly, which may have then limited the primary production or have controlled the phytoplankton species composition, even if the Mediterranean basin is one of the areas receiving the largest atmospheric inputs of desert dust in the world.

[37] The total Fe flux coming from the atmosphere during the mixing period corresponded to a DFe atmospheric flux of $23 \mu\text{mol m}^{-2}$ and to a DFe input of 0.12 nmol L^{-1} in the ML, which is \sim seven times lower than the DFe input recorded during the stratified period. This result is mainly due to a greater depth of the ML, which resulted in a dilution into a much large water body. It was also due to the total atmospheric flux itself, which was 4.5 times lower than that recorded during the stratified period (without taking into account the Saharan event that occurred on 26 February). As pointed out before, this large event represented 88% of the annual Fe flux, but the resulting DFe input related to it was only 0.02 nmol L^{-1} . A large storm associated with strong winds occurred just after this event, which caused a deep mixing of the water column down to a depth of 700 m, perhaps even to a depth of 900 m. These results indicate for the first time that the atmospheric influence on the DFe concentrations in seawater during fall and winter is extremely reduced compared to its influence during the stratified period.

4.3. Origin of the Atmospheric DFe (Saharan Versus Anthropogenic)

[38] We have shown that 44% of the DFe provided to the ML by atmospheric deposition during the stratified period was of anthropogenic origin in 2004. However, only 1% of the total annual atmospheric Fe flux was of anthropogenic

origin. This result can be explained by the difference of Fe lability in both types of aerosols. Bonnet and Guieu [2004] showed that the solubility of Fe contained in urban aerosols was twice as much in seawater as the solubility of Fe contained in Saharan dust. Many authors [Guieu *et al.*, 1994; Chester *et al.*, 1993] also reported the same feature for other metals (Mn, Cu, Zn and Pb). This higher solubility is due to the fact that metals are more exchangeable in anthropogenic particles, in which Fe is usually present under the form of exchangeable oxides located at the surface of the particles, than in mineral Saharan dust, in which most of the Fe is contained in refractory aluminosilicates. Moreover, the high surface to volume ratio of anthropogenic particles is more favorable to Fe dissolution because of their small size. Finally, the pH may influence the Fe dissolution: Polluted rains are known to be associated with low pH [see, e.g., Loye-Pilot and Morelli, 1988]. In contrast, Loye-Pilot *et al.* [1986] reported high pH in Saharan rains (due to the dissolution of CaCO_3 contained in desert dust). These effects may have respectively enhanced or reduced the Fe dissolution processes in the microenvironment of the particles.

4.4. Potential Impact on Biological Communities

[39] The new data presented here provide the first look at the Fe cycle on an annual basis in the Mediterranean Sea and its imprint on biological activity. Fe is the limiting nutrient that regulates ecosystem processes in many regions where a high nitrate concentration is present [see, e.g., Boyd *et al.*, 2000; Coale *et al.*, 1996]. Falkowski [1997] hypothesized that Fe may also regulate processes in low nitrate, oligotrophic regions by controlling the rate of nitrogen fixation. Aerosol deposition has been shown to drive large changes in *Trichodesmium* stocks in the Gulf of Mexico [Lenes *et al.*, 2001]. However, few studies [Bonnet *et al.*, 2005] have examined the impact of atmospheric Fe deposition on the phytoplanktonic dynamic in the Mediterranean Sea, a low nutrient low chlorophyll system that is submitted to high atmospheric deposition. The significant temporal variability of DFe concentrations in surface waters may nevertheless control the phytoplankton community structure in this area.

[40] Even if DFe profiles in the Mediterranean Sea have been reported to have a nutrient-like shape during the spring bloom [Sarthou and Jeandel, 2001], the covariation of DFe and macronutrients (N, P) during the summer and fall are in opposition, and from these observations we can expect a seasonal cycle of Fe limitation on algal growth in the Mediterranean Sea. In summer, high DFe concentrations accumulated in the surface ML combined with a limited supply of macronutrients from below (usually undetectable concentrations from June to November [Marty *et al.*, 2002]) should lead to a condition where biological growth is not Fe limited (Figure 4). In contrast, biological activity during the spring bloom can decrease surface water DFe to very low concentrations, to the point where subsequent algal growth is Fe limited. At that period, large cells (microphytoplankton) and nanophytoplankton dominate the phytoplanktonic community (Figure 4); large cells like diatoms have high Fe requirements: Blain *et al.* [2002] have reported half-saturation constant for growth (K_{μ}) up to 0.45 nmol L^{-1} for Southern Ocean diatoms. Such requirements (higher than

the DFe concentrations measured in surface waters at that period) could implicate that there is a Fe limitation that reduces the intensity of the bloom at the DYFAMED site.

[41] In contrast, during the stratified period, the phytoplankton biomass was characterized by an abundance of small-size phytoplankton (picophytoplankton) (Figure 4) with low nutrient requirements [Hein *et al.*, 1995]. During that period the Fe:N ratio exhibited a maximal value (≥ 0.02 in September), indicating an abundance of Fe compared to nitrogen in surface waters. In the framework of the same programme (MELISSA), nitrogen fixation rates have been measured (V. Sandroni *et al.*, Importance of diazotrophy and dry atmospheric inputs of nitrogen and phosphorus in the nutrient budget of the western Mediterranean Sea, submitted to *Deep Sea Res., Part I*, 2006) simultaneously to DFe concentrations. The highest rates of nitrogen fixation were obtained in August and were of the same order of magnitude than those measured in the North Atlantic and Pacific subtropical gyres [Capone *et al.*, 1997; Karl *et al.*, 1997]. Diazotrophs populations have Fe requirements 5 to 10 times greater than those for phytoplankton based on another source of nitrogen like ammonia [Kustka *et al.*, 2003]. The occurrence of high nitrogen fixation rates during the period of high DFe concentrations indicate that atmospheric DFe may participate to nitrogen fixation process. This hypothesis is in strong agreement with results from the enrichment experiment performed by Bonnet *et al.* [2005] at the DYFAMED site in August 2003 that indicates that an addition of Fe and Fe+phosphate could increase the primary production by 23% and 56%, respectively. The authors concluded that this ability to grow in an Fe-enriched/N-depleted environment could be explained by effective nitrogen fixation. Pigment analyses performed in these treatments indicated that this increase was mainly attributed to cyanobacteria, giving a strong argument in favor of this hypothesis.

[42] However, it should be noted that the pool of Fe accumulated during the stratified period did not constitute an entirely bioavailable pool for the biota. Wu *et al.* [2001] demonstrated that DFe may be less bioavailable to phytoplankton than previously thought. They showed that only a small fraction of the sea surface DFe in areas submitted to high atmospheric supply of Fe existed as soluble Fe (size fraction lower than $0.02 \mu\text{m}$); the other fraction is removed from surface waters by colloidal aggregation. Biological uptake of Fe may also be reduced if other factors are limiting the primary production. The high N:P ratio supports the assumption that P is a limiting factor in the Mediterranean Sea [Béthoux *et al.*, 1998]. Ridame and Guieu [2002] demonstrated that Saharan inputs also provide other dissolved components such as Dissolved Inorganic Phosphorus (DIP). They showed that this DIP has a negligible impact on the new production at the scale of the oligotrophic season. Using their parameterization, we have calculated that the total DIP input related to Saharan dust deposition during the stratified period was $\sim 0.9 \text{ nmol L}^{-1}$, but this pool must have been higher because anthropogenic particles have also been reported to be a source of DIP [Migon and Sandroni, 1999]. 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 ML [Ridame and Guieu,

2002]. Nitrogen fixation may be particularly stimulated by these inputs of both Fe and DIP as suggested by Bonin *et al.* [1989]. Saharan dust and anthropogenic particles have also been reported to be a source of DIN [Bonnet *et al.*, 2005]. These authors showed that a realistic fertilisation of dust during the stratified period resulted in an increase of 48% of the primary production, mainly associated to eukaryotic populations.

5. Conclusions

[43] These data provide the first study of the coupling between atmospheric and marine Fe cycle in the Mediterranean environment and confirm the significance of the atmospheric inputs in the control of the surface Fe concentrations. Atmospheric input of dissolved iron was estimated (from total atmospheric deposition) to be $42 \mu\text{mol m}^{-2} \text{ yr}^{-1}$ in the Ligurian Sea. We have demonstrated that the seasonal variability of atmospheric DFe concentrations in surface waters was driven by a combination of factors, including aeolian Fe deposition, nature of aerosols, vertical mixing, phytoplankton uptake, and particle scavenging. In 2004, the higher atmospheric imprint occurred during the stratified period, when the surface waters were isolated from deeper ones, which resulted in an accumulation of atmospheric DFe in surface waters of 0.88 nmol L^{-1} . Despite the paucity of anthropogenic aerosol deposition compared to Saharan dust, we have demonstrated that the labile Fe oxides contained in these polluted particles accounted for a significant part of the total DFe accumulation during the stratified period. From our observations we hypothesized that abundant DFe in the ML during the stratified period (high Fe:N ratio) can enhance the nitrogen fixation process. In contrast, we suspect that low DFe could reduce the intensity of the bloom during spring bloom. This study thus demonstrates that annual Fe distribution can have a clear biogeochemical effect on the autotrophic communities in low nutrient low chlorophyll systems such as the Mediterranean Sea. It is thus important to predict the long term variability of atmospheric deposition of Fe in order to better understand the evolution of the marine ecosystem.

[44] Dust is derived from arid and semiarid regions, most of which are found in the midlatitudes of the Northern Hemisphere [Schutz *et al.*, 1990]. Goudie and Middleton [1992] suggested that human soil disturbance can affect the production of atmospheric dust and Tegen *et al.* [1996] showed in their model that $50 \pm 20\%$ of the global dust flux arises from disturbed soils. By comparison, model projections suggest that the anthropogenic emissions might increase by a factor of 3 to 4 in 2020 relative to 1980 in the coastal ocean and somewhat lower in the open ocean [Galloway *et al.*, 1994]. These human perturbations will certainly enhance DFe concentrations in the global ocean, altering in turn its biogeochemical functioning.

[45] **Acknowledgments.** This work is part of the doctoral dissertation of S. Bonnet (grant of the French Ministère de l'Éducation Nationale, de l'Enseignement Supérieur et de la Recherche). The survey at the DYFAMED site was performed within the framework of the French program PROOF, Opération MELISSA: Méditerranée Limitations Saisonnières. We thank C. Migon, responsible for this operation, and J.C. Marty, responsible for the French DYFAMED time series, as well as the captain and crew of the *Tethys II* for their cooperative work at sea. We also thank N. Leblond and T. Wagener for their help at sea, M.D. Loye-Pilot for her

advice on atmospheric data processing, L. Prieur for his helpful suggestions on physical data interpretation, A. Dufour for digestions and ICP measurements, and D. Tailleux for the CTD data.

References

- Andersen, V., and L. Prieur (2000), One-month study in the open NW Mediterranean Sea (DYNAPROC experiment, May 1995): Overview of the hydrobiogeochemical structures and effects of wind events, *Deep Sea Res., Part I*, 47, 397–422.
- Beauvais, S. (2003), Etude des Particules Expolymeriques Transparentes (TEP) en milieu marin. Dynamique et rôle dans le cycle du carbone, Ph.D. thesis, 256 pp., U. Pierre et Marie Curie, Paris.
- Béthoux, J. P., P. Morin, C. Chaumery, O. Connan, B. Gentili, and D. Ruiz-Pino (1998), Nutrients in the Mediterranean Sea, mass balance and statistical analysis of concentrations with respect to environmental change, *Mar. Chem.*, 63, 155–169.
- Blain, S., P. N. Sedwick, F. B. Griffiths, B. Queguiner, E. Bucciarelli, M. Fiala, P. Pondaven, and P. Tréguer (2002), Quantification of algal iron requirements in the subantarctic Southern Ocean, *Deep Sea Res., Part II*, 49, 3255–3274.
- Blain, S., C. Guieu, H. Claustre, K. Leblanc, T. Moutin, B. Queguiner, and G. Sarthou (2004), Availability of iron for phytoplankton in the north-east Atlantic Ocean, *Limnol. Oceanogr.*, 49, 2095–2104.
- Bonin, D. J., M. C. Bonin, and T. Berman (1989), Mise en évidence expérimentale des facteurs nutritifs limitants de la production du micro-nanoplancton et de l'ultraplancton dans une eau côtière de la Méditerranée orientale (Haïfa, Israël), *Aquat. Sci.*, 51, 129–152.
- Bonnet, S., and C. Guieu (2004), Dissolution of atmospheric iron in seawater, *Geophys. Res. Lett.*, 31, L03303, doi:10.1029/2003GL018423.
- Bonnet, S., C. Guieu, J. Chiaverini, J. Ras, and A. Stock (2005), Effect of atmospheric nutrients on the autotrophic communities in a low nutrient, low chlorophyll system, *Limn. Oceanogr.*, 50, 1810–1819.
- Boyd, P. W., et al. (2000), A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization, *Nature*, 407, 695–702.
- Boyle, E., B. A. Bergquist, R. A. Kayser, and N. Mahowald (2005), Iron, manganese, and lead at Hawaii Ocean Time-series station ALOHA: Temporal variability and an intermediate water hydrothermal plume, *Geochim. Cosmochim. Acta*, 69, 933–952.
- Bruland, K. W., E. L. Rue, and G. J. Smith (2001), Iron and macronutrients in California coastal upwelling regimes: Implications for diatom blooms, *Limnol. Oceanogr.*, 46, 1661–1674.
- Capone, D. G., J. P. Zehr, H. W. Paelr, B. Bergman, and E. J. Carpenter (1997), Trichodesmium, a globally significant marine cyanobacterium, *Science*, 276, 1221–1229.
- Chester, R., K. J. T. Murphy, F. J. Lin, A. S. Berry, G. A. Bradshaw, and P. A. Corcoran (1993), Factors controlling the solubilities of trace metals from non-remote aerosols deposited to the sea surface by the “dry” deposition mode, *Mar. Chem.*, 42, 107–126.
- Chester, R., M. Nimmo, and S. Keyse (1996), The influence of Saharan and Middle Eastern desert-derived dust on the trace metal composition of Mediterranean aerosols and rainwater: An overview, in *The Impact of Desert Dust Across the Mediterranean*, edited by S. Guerzoni and R. Chester, pp. 253–273, Springer, New York.
- Coale, K. H., et al. (1996), A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean, *Nature*, 383, 495–501.
- Colin, J. L., J. L. Jaffezzo, and J. M. Gros (1990), Solubility of major species in precipitation: Factors of variation, *Atmos. Environ.*, 24A, 537–544.
- de Baar, H. J. W., and J. T. M. de Jong (2001), Distributions, sources and sinks of iron in seawater, in *Biogeochemistry of Iron in Seawater*, edited by D. R. Turner and K. A. Hunter, pp. 123–253, John Wiley, Hoboken, N. J.
- Falkowski, P. G. (1997), Evolution of the nitrogen cycle and its influence on the biological sequestration of CO₂ in the ocean., *Nature*, 387, 272–275.
- Galloway, J. N., H. I. Levy, and P. S. Kasibhatla (1994), Year 2020: Consequences of population growth and development on deposition of oxidized nitrogen, *Ambio*, 23, 120–123.
- Gouldie, A. S., and N. J. Middleton (1992), The changing frequency of dust storms through time, *Clim. Change*, 20, 197–225.
- Guerzoni, S., et al. (1999), The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea, *Prog. Oceanogr.*, 44, 147–190.
- Guieu, C., R. Duce, and R. Arimoto (1994), Dissolved input of manganese to the Ocean: Aerosol source, *J. Geophys. Res.*, 99, 18,789–18,800.
- Guieu, C., R. Chester, M. Nimmo, J. M. Martin, S. Guerzoni, E. Nicolas, J. Mateu, and S. Keyse (1997), Atmospheric input of dissolved and particulate metals to the northwestern Mediterranean, *Deep Sea Res., Part II*, 44, 655–674.
- Guieu, C., M. D. Loye-Pilot, C. Ridame, and C. Thomas (2002a), Chemical characterization of the Saharan dust end-member: Some biological implications for the western Mediterranean Sea, *J. Geophys. Res.*, 107(D15), 4258, doi:10.1029/2001JD000582.
- Guieu, C., Y. Bozec, S. Blain, C. Ridame, G. Sarthou, and N. Leblond (2002b), Impact of high Saharan dust inputs on dissolved iron concentrations in the Mediterranean Sea, *Geophys. Res. Lett.*, 29(19), 1911, doi:10.1029/2001GL014454.
- Guieu, C., S. Bonnet, T. Wagener, and M. D. Loye-Pilot (2005), Biomass burning as a source of dissolved iron to open ocean?, *Geophys. Res. Lett.*, 32, L19608, doi:10.1029/2005GL022962.
- Hein, M., M. E. Pedersen, and K. Sand-Jensen (1995), Size-dependent nitrogen uptake in micro- and macroalgae, *Mar. Ecol. Prog. Ser.*, 118, 247–253.
- Hutchins, D. A., et al. (2002), Phytoplankton iron limitation in the Humboldt current and Peru upwelling, *Limnol. Oceanogr.*, 47(4), 997–1010.
- Jickells, T. D., et al. (2005), Global iron connections between desert dust, ocean biogeochemistry, and climate, *Science*, 308, 67–71.
- Johnson, K. S., R. M. Gordon, and H. Coale (1997), What controls dissolved iron concentrations in the world ocean?: Author's closing comments, *Mar. Chem.*, 57, 181–186.
- Johnson, K. S., et al. (2003), Surface ocean-lower atmosphere interactions in the northeast Pacific ocean gyre: Aerosols, iron, and the ecosystem response, *Global Biogeochem. Cycles*, 17(2), 1063, doi:10.1029/2002GB002004.
- Karl, D., R. Letelier, L. Tupas, J. Dore, J. Christian, and D. Hebel (1997), The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean, *Nature*, 388, 533–538.
- Kustka, A. B., E. J. Carpenter, S. Sañudo-Wilhelmy, and W. G. Sunda (2003), Iron requirements for N₂ and NH₄⁺ supported growth in cultures of *Trichodesmium* (IMS 101): Comparison with nitrogen fixation rates and Fe:C ratios of field populations, *Limnol. Oceanogr.*, 48, 1869–1884.
- Lenes, J. M., et al. (2001), Iron fertilization and the *Trichodesmium* response on the west Florida shelf, *Limnol. Oceanogr.*, 46, 1261–1277.
- Levy, M., L. Memery, and J. M. André (1998), Simulation of primary production and export fluxes in the northwestern Mediterranean Sea, *J. Mar. Res.*, 56, 197–238.
- Loye-Pilot, M. D., and J. M. Martin (1996), Saharan dust input to the western Mediterranean: An eleven year record in Corsica, in *The Impact of Desert Dust Across the Mediterranean*, edited by S. Guerzoni and R. Chester, pp. 191–199, Springer, New York.
- Loye-Pilot, M.-D., and J. Morelli (1988), Fluctuations of ionic composition of precipitations collected in Corsica related to changes in the origins of incoming aerosols, *J. Aerosol Sci.*, 19, 577–585.
- Loye-Pilot, M. D., J. M. Martin, and J. Morelli (1986), The influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean, *Nature*, 321, 427–431.
- Martin, J. H., et al. (1994), Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean, *Nature*, 371, 123–129.
- Marty, J. C., J. Chiaverini, M. D. Pizay, and B. Avril (2002), Seasonal and interannual dynamics of nutrients and phytoplankton pigments in the western Mediterranean Sea at the DYFAMED time-series station (1991–1999), *Deep Sea Res., Part II*, 49, 1965–1985.
- Michaels, A. F., D. Olson, J. L. Sarmiento, J. W. Ammerman, K. Fanning, R. Jahnke, A. H. Knap, F. Lipschultz, and J. M. Prospero (1996), Inputs, losses and transformation of nitrogen and phosphorus in the pelagic North Atlantic Ocean, *Biogeochemistry*, 35, 27–73.
- Migon, C., and V. Sandroni (1999), Phosphorus in rainwater: Partitioning inputs and impact on the surface coastal ocean, *Limnol. Oceanogr.*, 44, 1160–1165.
- Migon, C., V. Sandroni, J. C. Marty, B. Gasser, and J. C. Miquel (2002), Transfer of atmospheric matter through the euphotic layer in the northwestern Mediterranean: Seasonal pattern and driving forces, *Deep Sea Res., Part II*, 49, 2125–2141.
- Mills, M. M., C. Ridame, M. Davey, J. La Roche, and J. G. Geider (2004), Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic, *Nature*, 429, 292–294.
- Moulin, C., C. E. Lambert, F. Dulac, and U. Dayan (1997), Control of atmospheric export of dust from North Africa by the North Atlantic Oscillation, *Nature*, 387, 691–694.
- Obata, H., H. Karatani, and E. Nakayama (1993), Automated determination of iron in seawater by chelating resin concentration and chemiluminescence detection, *Anal. Chem.*, 5, 1524–1528.
- Ridame, C., and C. Guieu (2002), Saharan input of phosphorus to the oligotrophic water of the open western Mediterranean, *Limnol. Oceanogr.*, 47, 856–869.
- Ridame, C., C. Guieu, and M.-D. Loye-Pilot (1999), Trend in total atmospheric deposition fluxes of aluminium, iron and trace metals in the north-western Mediterranean, over the past decade (1985–1997), *J. Geophys. Res.*, 104, 30,127–30,138.

- Sarthou, G., and C. Jeandel (2001), Seasonal variations of iron concentrations in the Ligurian sea and iron budget in the western Mediterranean Sea, *Mar. Chem.*, 74, 115–129.
- Sarthou, G., et al. (2003), Atmospheric iron deposition and sea-surface dissolved iron concentrations in the eastern Atlantic Ocean, *Deep Sea Res., Part I*, 50, 1339–1352.
- Schutysse, P., W. Maenhaut, and R. Dams (1978), Instrumental neutron activation analysis of dry atmospheric fallout and rainwater, *Anal. Chim. Acta*, 100, 75–85.
- Schutz, L. W., J. M. Prospero, P. Buat-Ménard, R. A. C. Carvalho, A. Cruzado, P. Harris, N. Z. Heidam, and R. Jaenicke (1990), The long range transport of mineral aerosols: Group report, in *The Long Range Transport of Natural and Contaminant Substances*, edited by A. H. Knap et al., *NATO ASI Ser.*, vol. 297, pp. 197–229, Springer, New York.
- Sigg, L. (1998), Partitioning of metals to suspended particles, in *Metals in Surface Waters*, edited by A. W. G. Herbert, E. Allen, and W. George Luther, pp. 217–239, Sleeping Bear Press, Chelsea, Mich.
- Spokes, L. J., and T. D. Jickells (1996), Factors controlling the solubility of aerosol trace metals in the atmosphere and on mixing into seawater, *Aquat. Geochem.*, 1, 355–374.
- Statham, P. J., and V. Hart (2005), Dissolved iron in the Cretan Sea (eastern Mediterranean), *Limnol. Oceanogr.*, 50, 1142–1148.
- Stemmann, L., G. Gorsky, J. C. Marty, M. Picheral, and J. C. Miquel (2002), Four year study of large-particle vertical distribution (0–1000 m) in the NW Mediterranean in relation to hydrology, phytoplankton, and vertical flux, *Deep Sea Res., Part II*, 49, 2143–2162.
- Tegen, I., A. Lacis, and I. Fung (1996), The influence on climate forcing of mineral aerosol from disturbed soil, *Nature*, 380, 419–422.
- Vidussi, F., H. Claustra, B. Manca, A. Luchetta, and J. C. Marty (2001), Phytoplankton pigment distribution in relation to the upper thermocline circulation in the eastern Mediterranean Sea during winter, *J. Geophys. Res.*, 106, 19,939–19,956.
- Wu, J., E. Boyle, W. G. Sunda, and L. S. Wen (2001), Soluble and colloidal iron in the oligotrophic North Atlantic and North Pacific, *Science*, 293, 847–849.

S. Bonnet and C. Guieu, Laboratoire d’Océanographie de Villefranche, La darse BP 08 06238 Villefranche sur mer, France. (sbonnet@obs-vlfr.fr)