Atmos. Meas. Tech. Discuss., 8, 2299–2329, 2015
www.atmos-meas-tech-discuss.net/8/2299/2015/
doi:10.5194/amtd-8-2299-2015

Atmospheric Measurement Techniques Discussions

An automatic collector to monitor insoluble atmospheric deposition: an application for mineral dust deposition

B. Laurent[1], R. Losno[1,*], S. Chevaillier[1], J. Vincent[1], P. Roullet[2], E. Bon Nguyen[1], N. Ouboulmane[1], S. Triquet[1], M. Fornier[3], P. Raimbault[3], and G. Bergametti[1]

[1]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR7583 CNRS, Université Paris 7 Denis Diderot, Université Paris-Est Créteil, Institut Pierre-Simon Laplace, France
[2]Ingénierie, Conseil, Assistance technique, Recherche, Etude (ICARE Ingénierie), Paris, France
[3]Mediterranean Institute of Oceanography (MIO), UMR7294 CNRS, UMR235 IRD, Université Aix-Marseille, Université du Sud Toulon-Var, France
[*]now at: Institut de Physique du Globe de Paris (IPGP), UMR7154 CNRS, Sorbonne Paris Cité, Université Paris 7 Denis Diderot, France

Received: 23 December 2014 – Accepted: 18 February 2015 – Published: 2 March 2015

Correspondence to: B. Laurent (benoit.laurent@lisa.u-pec.fr)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Deposition is one of the key processes controlling the mass budget of the atmospheric mineral dust concentration. However, dust deposition remains poorly constrained in transport models simulating the atmospheric dust cycle. This is mainly due to the limited number of relevant deposition measurements. This paper aims at presenting an automatic collector (CARAGA), specially developed to sample the total (dry and wet) atmospheric deposition of insoluble dust in remote areas. The autonomy of the CARAGA can range from 25 days to almost 1 year depending on the programed sampling time step (1 day and 2 weeks sampling time steps, respectively). This collector is used to sample atmospheric deposition on Frioul Island which is located in the Gulf of Lions in the Western Mediterranean Basin over which Saharan dust can be transported and deposited. To quantify the mineral dust mass in deposition samples, a weighing and ignition protocol is applied. Two years of continuous deposition measurements performed on a weekly time step sampling on Frioul Island are presented and discussed with in-situ measurements, air mass trajectories and satellite observations of dust.

1 Introduction

Mineral dust particles emitted from the Sahara can contribute to be the exceedance of daily air quality threshold values of particulate matter with aerodynamic diameter below 10 µm ($PM_{10} > 50\,\mu g\,m^{-3}$) observed in the Mediterranean Basin and Southern Europe (Pey et al., 2013). In order to estimate these Saharan dust outbreaks over this region, Chemistry–Transport Models (CTM) could provide continuous and forecasted fields of dust concentration. Simulations of mineral dust are currently validated by comparing the simulated dust load with numerous available datasets, as for instance direct aerosol concentration measurements and aerosol optical depth (AOD) derived from ground based and/or satellite observations. But this remains insufficient to ensure the consistency of regional or global dust simulations, since, due to the lack of quantitative

AMTD
8, 2299–2329, 2015

measurements, emission and deposition can be tuned quite freely to allow models to match observed atmospheric dust concentrations. This means that at least one additional term, emission or deposition mass flux, has to be measured to constrain correctly the simulated dust mass budget.

Large uncertainties remain, for instance, on how dry and wet dust deposition processes are modelled (Zhao et al., 2003; Textor et al., 2006; Jung and Shao, 2006; Bergametti and Forêt, 2014). Few experimental field measurements of dust deposition were performed recently (Guieu et al., 2010; López-Garcia et al., 2013; Heimburger et al., 2013; Osada et al., 2014). Accurate measurements of dust mass fluxes remain scarce whereas they should be done continuously and homogenously over regions impacted by mineral dust in order to constrain model dust simulations. One of the reasons why such a small number of field studies has been performed is the heavy workload that represent both sampling and measurement of dust deposition over long periods of time.

This paper presents a new device designed to perform continuous dust deposition measurements on long time series and a weighing and ignition protocol to determine the total insoluble mineral dust mass deposited. These measurements can be used to constrain deposition processes in CTM. This automatic collector, named CARAGA (Collecteur Automatique de Retombées Atmosphériques insolubles à Grande Autonomie), is specially developed to sample total insoluble atmospheric particles deposition in remote areas, and to insure robust automatic sampling with a large autonomy and a minimum need of man power. Since mid-2010, total deposition (dry and wet) is installed on Frioul Island (43.27° N; 5.29° E) which is located in the Gulf of Lions, in the north-western Mediterranean Sea where Saharan dust outbreaks can be observed (see for example Ridame et al., 1999). The in-situ deposition sampling strategy is presented, as well as the lab protocol established to quantify mineral dust deposition. The first 2 yr of total mineral deposition measurements on Frioul Island are discussed and pointed out the feasibility of the use of CARAGA collectors to develop a sampling network of total insoluble deposition in remote area.

AMTD
8, 2299–2329, 2015

2 Previous studies of dust deposition sampling

Dry deposition depends mainly on sedimentation, interception, impaction and brownian diffusion processes (Slinn and Slinn, 1980; Wesely, 1989; Venkatram and Pleim, 1999). Wet deposition processes correspond to the capture of particles by droplets either inside or below the clouds (Dana and Hales, 1976; Slinn, 1984; Garcia Nieto et al., 1994). These deposition processes of atmospheric particles are supposed to be well understood. However, most of the theoretical understanding and parameterizations of deposition were developed based on studies and measurements performed under controlled conditions, for instance in wind tunnels (Chamberlain, 1967; Goossens, 2008) or tower laboratories (Wang and Pruppacher, 1977; Leong et al., 1982; Barlow and Latham, 1983; Pranesha and Kamra, 1996).

In-situ dust deposition measurements of atmospheric particles are technically difficult and have to be adapted depending on the aim of the study: dry, wet or total deposition; soluble, insoluble or bulk deposition; with a short time step sampling or over long time period, etc. Quantitative estimates of dust deposition remain thus challenging (see for example Wiggs et al., 2002; Goossens and Rajot, 2008). Various techniques have been proposed to directly measure or to estimate (from atmospheric concentrations) the dry deposition of dust on surfaces (Seinfeld and Pandis, 1998; Etyemezian et al., 2003; Goossens, 2005; Sow et al., 2006). Experimental studies usually show a wide range in dry deposition values, depending on the sampling device (Goossens and Rajot, 2008). Even if wet deposition measurements are easier to perform, correctly sampling the first mm of a precipitation event is crucial to measure precisely the wet deposition (Claassen and Halm, 1995). In the framework of this study, the sampling of total (dry and wet) Saharan dust deposition is investigated.

Up to now, Saharan dust deposition sampling required frequent human intervention to be carried out. Most of the time deposition collectors consist in simple passive collecting systems: funnel capped bottles (Markaki et al., 2010; Prospero et al., 2010), polyethylene bottles (Bonnet and Guieu, 2006; Markaki et al., 2010), bags (Galy-

AMTD
8, 2299–2329, 2015

Lacaux et al., 2009) and buckets (Prospero et al., 2010), or surfaces covered with glass marbles (Kouvarakis et al., 2001; Sow et al., 2006). Similar collectors have been used to sample mineral dust in other regions, as for example in Asia by Osada et al. (2014) or on the Kerguelen Island in the Southern Ocean (Heimburger et al., 2013). None of these collecting systems allows sampling dust deposition automatically and/or with a sufficient autonomy in order to limit human intervention after each sampling time step.

In the Mediterranean Basin, Saharan dust deposition was sampled in Capo Cavallo (NW Corsica) using a CRAPAL sampler (Bergametti, 1987; Remoudaki et al., 1991). It is a hemispheric plexiglass collection device (0.1 m^2), with a 10 cm-high neck, covered by a 1 mm nylon mesh (Lambert and Nezami, 1965). Its base is connected to an acid cleaned polyethylene bucket in which the atmospheric deposition is collected during precipitation and by manual acid flushing at the end of a one week sampling period. Loÿe-Pilot and Martin (1996) also collected Saharan dust deposition in Corsica during a 11 yr period (1984–1994) using a bulk plastic collector (Standard Rain Gauge) having a 400 cm^2 aperture. Deposition measurements were also performed on the two sides of the Ligurian Sea at the Cap Ferrat Site in 2004 and 2006 (Bonnet and Guieu, 2006; Pulido-Villena et al., 2008) and in Corsica in 2003 and 2005 (Ternon et al., 2010) using the same bulk plastic collector or a funnel and a polyethylene bottle. The most comprehensive program to assess the magnitude and the composition of atmospheric deposition in the Mediterranean Basin was the ADIOS program during which atmospheric deposition were collected at 10 sampling sites (Guieu et al., 2010; Markaki et al., 2010). The mass of the deposited Saharan dust was deduced from the measured Al amount. The sampling device collected bulk samples (dry and wet deposition) using a 1 gallon Nalgene high density polyethylene (HDPE) bottle, with a polyethylene funnel (0.011 m^2) attached on its top. The sampling was performed with a one month time step period and required human intervention.

Dust total deposition was also collected in the Sahelian region using a CAPYR sampler (Orange et al., 1990; Herrmann, 1996; Rajot, 2001). The CAPYR is a 40 cm high, funnel-shaped sampler with a 0.25 m^2 horizontal inlet opening. Total dust deposition

AMTD
8, 2299–2329, 2015

was collected in Niger from 1996 to 1998 (Rajot, 2001). In Niger, a Frisbee sampler, which consists in a circular stainless steel collecting bowl (0.07 m^2) and 3.6 cm deep, surrounded by an aerodynamically shaped aluminum deflector ring (Wiggs et al., 2002), was also used to collect total dust deposition (Sow et al., 2006). Manual rinsing is required to collect the total deposition.

To collect dry and wet Saharan dust deposition separately, ARS MTX or Aerochem Metrics model 301 samplers were used on the Eastern and Western Mediterranean coasts (Ozsoy, 2003; Morales-Baquero et al., 2013) and on the Canary Islands (López-Garcia et al., 2013). To perform successive samples, the collect systems have to be manually replaced. Wet deposition was also collected with wet-only collectors in Eastern Mediterranean (Theodosi et al., 2010), in Niger (Galy-Lacaux et al., 2009) and in Florida (Prospero et al., 2010). The conservation of the deposition soluble fraction in time strongly limits the autonomy of the sampling device.

These various approaches (and associated samplers) have technical drawbacks on the field that have limited their development in terms of sampling network expansion or duration, especially due to a short autonomy, as human intervention is always required to replace the collect system after each sample time step. A robust automatic system is therefore necessary to achieve a low cost long term and wide area network survey system.

3 New sampler and method to study mineral dust deposition

3.1 The CARAGA collector

The existing deposition samplers are not automatized and/or not autonomous over long periods. This constitutes a strong limitation to perform continuous long term in-situ measurements of atmospheric deposition in remote areas. The ICARE Ingénierie Company and the Laboratoire Interuniversitaire des Systèmes Atmosphériques developed a collector, the CARAGA (Collecteur Automatique de Retombées Atmosphériques in-

AMTD
8, 2299–2329, 2015

solubles à Grande Autonomie) to automatically sample the total insoluble deposition on filters over long periods without any human intervention. The domain of application of this collector is to provide an estimate of the mass of deposited dust during a given time period, mainly to better constrain CTM dust cycle simulations. By focusing on the total insoluble mass of deposited dust, the sampling device can be significantly simplified, and the issues associated to the change and the storage of the samples are limited. In order to estimate the deposited mass, collecting only the insoluble part of the dust deposition is justified by the very large fraction of the insoluble matter in the Saharan dust deposition, larger than 80 % of the total mass in the Mediterranean Basin (see for example Losno, 1989; Guerzoni et al., 1993; Avila et al., 2007).

The CARAGA was designed as separate modules making easier its transportation and in-situ implementation (see the Supplement). An open circle funnel (0.2 m^2) forms the top part of the CARAGA collector (Fig. 1). The collecting surface is a compromise to assure a sampling sufficient during low intensity deposition event and to avoid the saturation of the collecting filter in case of huge deposition event. Local soil dust contamination can be a problem for deposition measurements, especially during period of high wind speed. In order to minimize this contamination, the funnel is fixed on a steel structure and an adjustable tripod 2.5 to 3 m above the ground (Fig. 1). If the temperature drops down 2 °C, the funnel walls are heated with heating tapes. The funnel is connected using a short tube to a 25 holes carousel which carries filters mounted in separate filter holders (Figs. 1 and 2).

Two hours and one hour before the end of each sampling period, a device vibrates the funnel walls and 100 mL pure water, or a blend of 20 % ethanol in pure water in case of frost, is sprayed to drive down the atmospheric deposited particles and collect them on a 47 mm diameter membrane filter. This sample procedure is identically reproduced for each sample and does not require any operator intervention. Rain events are directly collected by the funnel. The filtration is performed by gravity and only the insoluble matter is collected on the filter, the remaining water being rejected. An electronic system controls the water level in the filter holder and periodically closes a pinch

AMTD
8, 2299–2329, 2015

valve installed on the tube at the bottom of the funnel if this level is too high. This is necessary to avoid water overflow of the filter holder and then the loss of a part of the wet deposition in case of heavy rain.

Twenty five filters previously prepared in the lab are installed in filter holders on the motorized carousel (Fig. 2). A new filter is set automatically in the sampling position for each sampling time step. This time step for sampling can be programmed and the autonomy of the instrument can range from 25 days for a 1 day sampling time step to almost 1 year for a 2 weeks sampling time step. An electronic recorder allows to store the date at which the rotating unit has worked for a post-control purpose. A solar panel (20 W) connected to a battery (12 V, 7 Ah) supplies the power.

3.2 Filter choice

The mass of mineral dust is considered to be dominated by the large particles contributing to $PM_{2.5}$ and PM_{10} mass budget. In order to choose the optimal filter to collect dust deposition several tests are performed. Because filtration is gravity driven only, the water flow through different filter membranes composed of polycarbonate, quartz or cellulose is tested: (i) AOX Nuclepore© polycarbonate filter (⌀ 47 mm, 0.4 µm porosity), (ii) nylon filters (⌀ 47 mm, 0.45 µm porosity), (iii) cellulose nitrate filter (⌀ 0.47 mm, 0.8 µm porosity), (iv) AA Millipore© cellulose ester filters (⌀ 47 mm, 0.8 µm porosity), (v) QMA Whatman© quartz fiber filter (⌀ 47 mm, 2.2 µm porosity). The test consists in determining the time required to drain 100 mL of pure water through the filter for a total volume of 200 mL. The AA Millipore cellulose ester filter with a 0.8 µm porosity is the only filter type for which a reasonable flow speed is obtained, about 20 mL min^{-1} (Table 1).

To test a possible mass loss by dissolution of the filter in water, six cellulose ester blank filters are weighed before and after filtration of 250 mL of pure water. In this study, all the weighings are done using a Mettler© AE240 electronic microbalance (sensitivity 10^{-4} g). For the weighing of the filters, an aluminium crucible is used to prevent electro-

AMTD
8, 2299–2329, 2015

static issues. Each sample is weighed until obtaining two equal successive displayed values. After filtration, different treatments are tested (1 h in an oven at 40 °C, 3 h in an oven at 40 °C, 17 h at ambient T °C, and 23 h at ambient T °C). The results show a mass variation of $\pm 3 \times 10^{-4}$ g.

3.3 Weighing and ignition protocol

To correctly quantify the deposited mass of mineral dust, an adapted protocol that accounts for the complex blending of particles constituting the atmospheric particulate deposition has to be defined.

The weighing of the first in-situ filters collected reveals specific constraints. The collected particles can have a diameter up to 10 µm, and therefore may not strongly adhere to the filter. Loss of particles during filter handling is possible, especially for filters highly loaded with particles. Furthermore, the aim of the present study being to characterize the deposition of Saharan dust particles, the presence of particles derived from emissions of pollutants or having a biogenic origin (e.g. organic aerosols) can affect the estimate of the mass of deposited mineral particles.

In order to eliminate the organic fraction of a sample, ignition protocols with temperatures ranging from 375 to 850 °C were used in previous studies (Ball, 1964; Hoenig and Thomas, 2002; Sun et al., 2009). This kind of protocol has the advantage to reduce the filter handling and to eliminate the deposited particles having medium to high volatility, as it is the case for most of organic aerosols.

A weighing protocol after ignition of the samples is followed in the present study. First, blank filters are placed in ceramic crucibles with their lids ajar in an ashing furnace (Naberthem© LT15/11). Various programs of temperature increase to reach 350, 550 and 950 °C are tested. To prevent a flame that can lead to the loss of material from the crucible during the calcination, the tests point out the necessity to control the temperature increase between 200 and 350 °C at a rate of 1 °C min^{-1}. The residual ash mass of the filters is weighed after different cycles of ignition at 350, 550 and 950 °C. The calcination of AA Millipore© cellulose ester blank filters showed their com-

AMTD
8, 2299–2329, 2015

plete destruction between 350 and 550 °C. Two triplicates of this test are performed and consecutive weighings are done to insure the balance instability. There is no detectable residue of the filter by weighing after ignition.

Comparative tests between direct weighings and weighings after ignition at 350, 550 and 950 °C are performed using (i) proxys of mineral dust prepared on filters by sieving a desert erodible soil collected in Douz (Tunisia) and a loess soil collected on Sal Island (Cape Verde), as well as (ii) the first filters collected at the Frioul site. Each filter is first weighted alone, before and after sampling, and then in its crucible with lid before and after ignition.

Three filters of the Douz sieved soil (0.126, 0.133 and 0.257 g) and three filters of the Cape Verde sieved loess (0.012, 0.012 and 0.015 g) are prepared after a passive filtration of the soil samples suspended in a water solution. The results of direct weighing as well as weighing of the samples after calcination at 350, 550 and 950 °C are gathered in Table 2. At 350 °C, filters residues are still present and contribute to the mass of the sample. This is no longer the case at 550 and 950 °C. The masses of the samples are lower after ignition at 550 °C than the initial masses (Douz 1: −3.2 %, Douz 2: −4.5 % and Douz 3: −2.3 %; Cape Verde 1: −8.3 %, Cape Verde 2: −8.3 %, Cape Verde 3: −13.3 %). This tendency is reinforced at 950 °C (Table 2). The same tests are done for samples collected on Frioul Island (Table 3). For the three filters with deposition masses varying over an order of magnitude (F7 = 0.011 g, F8 = 0.091 g, and F9 = 0.145 g), a greater loss on ignition is observed at 550 °C (18.2, 9.9 and 9.6 %, respectively) compared to the samples from Douz and Cape Verde. The six other filters showed no detectable deposition but allow testing the repeatability and the uncertainty of the method used to determine the mass of mineral deposit after ignition.

These tests point out that a temperature of 550 °C insures the loss on ignition of the filter, and of the organic matter which is destroyed below 450 °C (Hoenig and Thomas, 2002). Moreover, Sun et al. (2009) recorded only a small mass loss (lower than 0.2 %) for the quartz and feldspar during ignition at 550 °C. For minerals, mass losses lower than 0.2 % for the calcite and hematite, between 1 and 2.5 % for the smectite, chlorite,

AMTD
8, 2299–2329, 2015

illite and goethite, and up to 18 % for the kaolinite were observed (Sun et al., 2009). These authors showed that the structural water loss for 17 soil samples ranges from 0.56 to 2.45 % at 550 °C. This is consistent with the mass loss results obtained for the Douz soil which contains a significant proportion of quartz and calcite (Lafon et al., 2014). The larger mass loss observed for the Cape Verde soil can be partly due to its composition of quartz, potassic feldspars, and an assemblage of illite-kaolinite-chlorite (Rognon et al., 1996; Desboeufs et al., 1999). The larger loss on ignition observed for the atmospheric deposition suggests a higher fraction of volatile compounds in the Frioul samples than in the tested soils.

The maximum temperature of 550 °C is chosen for the ignition protocol applied to the samples collected on filters. To allow a slow combustion of the membrane filter and the destruction of the organics, the heating is carried out in four time steps (Table 4): 1st segment from 20 to 200 °C in 40 min, 2nd segment from 200 to 350 °C in 150 min, 3rd segment from 350 to 550 °C in 45 min, and 4th segment stabilized at 550 °C during 120 min. When the ignition protocol is finished, the crucibles are cooled down inside the furnace at ambient temperature.

To conclude, the direct weighing of filters and their weighing after ignition lead to the same level of accuracy with an uncertainty on the method used below 10^{-3} g. However, the direct weighing of filters is more restrictive for samples containing large amount of coarse particles and organic residues. The weighing after ignition limits the filter manipulations and thus the possible loss of a part of the sample. Moreover, this protocol allows focusing on the mineral fraction of the deposition, most of the organic particles being volatilized or oxidized when the final temperature reaches 550 °C.

4 Deposition measurements on Frioul Island

A CARAGA collector was installed mid-2010 on Frioul Island (43.27° N; 5.29° E), which is located 4 km in front of Marseille in the Gulf of Lions. One of the main constraints with Saharan dust sampling is that their transport from source regions towards the Mediter-

AMTD
8, 2299–2329, 2015

ranean Sea and Europe is sporadic. The sampling time should be short enough to catch dust transport events individually but long enough to provide a sufficient autonomy to the CARAGA. Dust fallout events are brief and usually less than 3 days long (Loÿe-Pilot and Martin, 1996). A sampling time step of one sample a week is adapted for collecting mineral particles corresponding to dust transport and deposition over the Mediterranean Basin. This time step also insures a large autonomy of the collector (up-to 25 weeks, depending on the number of in-situ blank filters intended).

In order to collect all the deposited particles on the filter, the funnel vibrating and rinsing with 100 mL of pure water are done twice (2 and 1 h before the filter change). To bring back the samples to the laboratory, a suitcase designed to keep the 25 filter holders with their lids in an upright position is used. Figure 3 visualizes the filters set collected on Frioul Island between July and December 2011. The various colors of the filters illustrate the difference in mass and the nature of the insoluble particulate deposition sampled from one week to another. The mineral masses of the weekly total (dry and wet) insoluble deposition for samples collected from February 2011 to October 2012 are reported in Fig. 4. The precipitation rates measured on Frioul Island are also presented in Fig. 4 in order to point out the potential wet deposition occurring during precipitation events.

The annual insoluble mineral deposition measured on Frioul Island is 2.45 $g\,m^{-2}$ for 2011 and 3.16 $g\,m^{-2}$ for 2012, which corresponds to low annual deposition amounts without very strong dust events in this area of the Mediterranean Basin. In fact, Loÿe-Pilot and Martin (1996) measured an average annual dust deposition dust flux of 12.5 $g\,m^{-2}$ in Corsica for an 11 yr period between 1984 and 1994, with annual deposition fluxes varying from 4.0 to 26.2 $g\,m^{-2}\,yr^{-1}$. They mentioned that high magnitude events drive the variability of the dust fallout at the annual and inter-annual scale. They also showed that more than 95 % of the Saharan events in Corsica are associated to wet deposition. Ternon et al. (2010) found an average annual deposition value of 11.4 $g\,m^{-2}$ at Cap Ferrat and Corsican sites between 2003 and 2006. Their measurements showed a high range of frequency and intensity of Saharan dust deposition

AMTD
8, 2299–2329, 2015

events: very low (5×10^{-2} g m^{-2}) dust flux events occurred relatively often (27 events in 4 years), and there was only one extreme event of 22 g m^{-2} representing almost 90 % of the deposition for 2004.

The weekly total insoluble deposition fluxes of mineral dust at the Frioul site also exhibit a large variability ranging over more than 2 orders of magnitude from 10^{-3} g m^{-2} to 3.3×10^{-1} g m^{-2} (Fig. 4). About 60 % of the measured deposition fluxes at the Frioul site are lower than 5×10^{-2} g m^{-2}. This indicates, that most of the time, the mineral deposition on Frioul Island can be attributed to low deposition due to atmospheric particles background. Nine major events with mineral deposition fluxes ranging from 1.5×10^{-1} to 3.3×10^{-1} g m^{-2} have been recorded on this site between (a) 7 and 14 July 2011, (b) 20 and 27 October 2011, (c) 26 April and 3 May 2012, (d) 17 and 24 May 2012, (e) 14 and 21 June 2012, (f) 28 June and 5 July 2012, (g) 23 and 30 August 2012, (h) 30 August and 6 September 2012, and (i) 27 September and 4 October 2012. In 2011 and 2012, the major deposition events occur more frequently in late spring and summer. Precipitations ranging from 1.0 to 80.8 mm are also measured on Frioul Island for 7 of these event periods (a, b, c, d, g, h and i), precipitation data being totally or partly missing for 2 event periods (e and f, respectively).

The monthly average insoluble deposition fluxes measured at the Frioul site from February 2011 to October 2012 are presented in Fig. 5. The range of these fluxes (from 100 to 470 mg m^{-2}) is comparable to the measurements previously performed in Cap Ferrat (Bonnet and Guieu, 2006; Pulido-Villena et al., 2008) in 2004 and 2006 and Corsica in 2003 and 2005 on both sides of the Ligurian Sea (see more details in Ternon et al., 2010). The measurements performed in Corsica between 1984 and 1994 by Loÿe-Pilot and Martin (1996) show higher monthly deposition amounts ranging from about 200 to 2500 mg m^{-2}. The monthly deposition measurements on Frioul Island show a maximum in early spring (April–May) in agreement with the measurements of Loÿe-Pilot and Martin (1996) in Corsica. Ternon et al. (2010) show maximum deposition in February due to a huge dust event and in late spring (June). These seasonal differences can be explained by the large dust deposition variability observed at the

AMTD
8, 2299–2329, 2015

event scale in the northern Mediterranean Basin (Loÿe-Pilot and Martin, 1996; Ternon et al., 2010).

For the major deposition events measured at the Frioul site, the aerosol optical depth (AOD) from MODIS AQUA and TERRA observations ranges from 0.4 to 0.8 suggesting high atmospheric loads in particulate matter. The origins of the air masses reaching the Frioul site for the 9 main deposition events measured are analyzed using the HYSPLIT model backward trajectories (https://ready.arl.noaa.gov/HYSPLIT.php) (Fig. 6). The HYSPLIT trajectories indicate air masses originating from the southern Mediterranean Basin and North-Africa for the major mineral deposition events (a, b, c, d, f, g and i) that have been recorded. For two events (e and h) the air mass trajectories suggest also an origin from the Mediterranean part but their pathways correspond more to a stagnant meteorological situation over the Gulf of Lions and the central part of the Western Mediterranean Basin.

5 Conclusions

An automatic collector (CARAGA) has been specially developed to sample total (dry and wet) insoluble atmospheric deposition and a protocol for the treatment of the collected samples implying ignition and weighing has been tested. This protocol allows focusing on the mineral fraction of the deposition, most of the organic particles being volatilized or oxidized at 550 °C.

An illustration of its use is provided through a study dealing with the estimate of Saharan dust deposition on Frioul Island, a site located in the Gulf of Lions. The collector worked continuously during two years and provided weekly total deposition samples. The annual insoluble mineral deposition measured on Frioul Island is 2.45 g m^{-2} for 2011 and 3.16 g m^{-2} for 2012, which corresponds to low annual deposition amounts without very strong dust events in the north-western Mediterranean Basin. The weekly deposited masses of insoluble mineral particles range over 2 orders of magnitude and nine major events with mineral deposition ranging from 1.5×10^{-1} to 3.3×10^{-1} g m^{-2} are

AMTD
8, 2299–2329, 2015

recorded on Frioul Island between February 2011 and October 2012. During this period, the major deposition events occurred more frequently during spring and summer. Precipitation, ranging from 1.0 to 80.8 mm, are associated to seven of these dust event periods, precipitation data having not totally or partly being recorded for the two other dust event periods. The nine major mineral deposition events measured are observed during periods for which aerosol optical depth from MODIS observations are high. Air masses passing over the Frioul site during these periods came from the Mediterranean Basin and North Africa. These elements strongly indicate that the higher deposition events measured on Frioul Island are due to Saharan dust transport associated to local precipitation.

In order to improve Saharan dust deposition monitoring in the Mediterranean Basin and the South of France, CARAGA collectors are now deployed over 8 stations located in France, Spain, Italy and Tunisia: Frioul (43.27° N; 5.29° E), Le Casset (44.99° N; 6.47° E), Montandon (47.28° N; 6.82° E), Cap Corse (43.00° N; 9.36° E), Mallorca (39.27° N; 3.05° E), Sierra Nevada (36.95° N; 3.43° W), Lampedusa (35.52° N; 12.63° E), and Medenine (33.50° N; 10.64° E). This network constitutes an operating and standardized network of total insoluble dust deposition. It should allow to document the pluriannual spatial and temporal variability of mineral dust deposition and to provide new constrains for CTM dust simulation over the Western Mediterranean region.

The Supplement related to this article is available online at doi:10.5194/amtd-8-2299-2015-supplement.

Acknowledgements. This study was funded by the PRIMEQUAL-ADEME program on "Pollution atmosphérique longue distance" through the research project "Mesure du dépôt atmosphérique et validation de sa représentation dans les modèles régionaux" (DEMO project, contract no. 0962c0067). This project was supported by the Chemistry Aerosol Mediterranean Experiment (ChArMEx project; http://charmex.lsce.ipsl.fr/) funded by CNRS/INSU, ADEME, Météo-

AMTD
8, 2299–2329, 2015

France and CEA in the framework of the programme MISTRALS (http://www.mistrals-home.org). The development of the CARAGA collector was supported both by the Chemistry Faculty of Paris Diderot University and the PRIMEQUAL-ADEME DEMO project. The authors thank François Dulac for fruitful discussions and comments. We thank the HYSPLIT teams for making the backward air mass trajectories available.

References

Avila, A., Alarcon, M., Castillo, S., Escudero, M., García Orellana, J., Masque, P., and Querol, X.: Variation of soluble and insoluble calcium in red rains related to dust sources and transport patterns from North Africa to northeastern Spain, J. Geophys. Res., 112, D05210, doi:10.1029/2006JD007153, 2007.

Ball, D. F.: Loss-on-ignition as an estimate of organic soils matter and carbon in-non calcareous soils, J. Soil Sci., 15, 84–92, 1964.

Barlow, A. K. and Latham, J.: A laboratory study of the scavenging of sub-micronaerosol by charged raindrops, Q. J. Roy. Meteorol. Soc., 109, 763–770, 1983.

Bergametti, G.: Apports de matière par voie atmosphérique à la Méditerranée Occidentale: aspects géochimiques et météorologiques, Thèse d'état, Univ. Paris VII, Paris, 296 pp., 1987.

Bergametti, G. and Forêt, G.: Dust deposition, in: Mineral Dust: a Key Player in the Earth System, edited by: Knippertz, P. and Stuut, J.-B. W., Springer, Dordrecht, 179–200, 2014.

Bonnet, S. and Guieu, C.: 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, 2006.

Chamberlain, A. C.: Transport of lycopodium spores and other small particles to rough surfaces, P. R. Soc. A, 296, 45–70, 1967.

Claassen, H. C. and Halm, D. R.: Performance characteristics of an automated wet deposition collector and possible effect on computed annual deposition, Atmos. Environ., 29, 1021–1026, 1995.

Dana, M. T. and Hales, J. M.: Statistical aspects of the washout of polydisperse aerosols, Atmos. Environ., 10, 45–50, 1976.

Desboeufs, K., Losno, R., Vimeux, F., and Cholbi, S.: The pH dependent dissolution of wind transported Saharan dust, J. Geophys. Res., 104, 21287–21299, 1999.

AMTD
8, 2299–2329, 2015

Etyemezian, V., Gillies, J., Kuhns, H., Nikolic, D., Watson, J., Veranth, J., Laban, R., Seshadri, G., and Gillette, D.: Field Testing and Evaluation of Dust Deposition and Removal Mechanisms: Final Report, Desert Research Institute, Las Vegas, NV, USA, 2003.

Galy-Lacaux, C., Laouali, D., Descroix, L., Gobron, N., and Liousse, C.: Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger), Atmos. Chem. Phys., 9, 1579–1595, doi:10.5194/acp-9-1579-2009, 2009.

Garcia Nieto, P. J., Arganza Garcia, B., Fernandez Diaz, J. M., and Rodriguez Brana, M. A.: Parametric study of selective removal of atmospheric aerosol by below-cloud scavenging, Atmos. Environ., 28, 2235–2342, 1994.

Goossens, D.: Quantification of the dry aeolian deposition of dust on horizontal surfaces: an experimental comparison of theory and measurements, Sedimentology, 52, 859–873, 2005.

Goossens, D.: Relationships between horizontal transport flux and vertical deposition flux during dry deposition of atmospheric dust particles, J. Geophys. Res., 113, F02S13, doi:10.1029/2007JF000775, 2008.

Goossens, D. and Rajot, J. L.: Techniques to measure the dry aeolian deposition of dust in arid and semi-arid landscapes: a comparative study in West Niger, Earth Surf. Proc. Land., 33, 178–195, doi:10.1002/esp.1533, 2008.

Guerzoni, S., Landuzzi, W., Lenaz, R., Quarantotto, G., Rampazzo, G., Molinaroli, E., Turetta, C., Visin, F., Cesari, G., and Cristini, S.: Fluxes of soluble and insoluble metals and nutrients from the atmosphere to the central Mediterranean Sea, Water Poll. R., 30, 438–493, 1993.

Guieu, C., Loÿe-Pilot, M. D., Benyaya, L., and Dufour, A.: Spatial variability of atmospheric fluxes of metals (Al, Fe, Cd, Zn and Pb) and phosphorus over the whole Mediterranean from a one-year monitoring experiment: biogeochemical implications, Mar. Chem., 120, 165–179, 2010.

Heimburger, A., Losno, R., Triquet, S., and Bon Nguyen, E.: Atmospheric deposition fluxes of 26 elements over the Southern Indian Ocean: time series on Kerguelen and Crozet Islands, Global Biogeochem. Cycles, 27, 440–449, 2013.

Herrmann, L.: Staubdeposition auf Böden West Afrikas, Eigenschaften und Herkunftsgebiete der Stäube und ihr Einfluss auf Böden und Standortseigenschaften, Ph. D. Thesis, Hohenheim Bodenkundliche Hefte 36, University of Hohenheim, Stuttgart, 1996.

AMTD
8, 2299–2329, 2015

Hoenig, M. and Thomas, P.: Préparation d'échantillons de l'environnement pour analyse minérale, Techniques de l'ingénieur Analyses dans l'environnement, Paris, vol. TIB382DUO, ref. p4150, 2002.
Jung, E. and Shao, Y.: An intercomparison of four wet deposition schemes used in dust transport modeling, Global Planet. Change, 52, 248–260, 2006.
Kouvarakis, G., Mihalopoulos, N., Tselepides, A., and Stavrakakis, S.: On the importance of atmospheric inputs of inorganic nitrogen species on the productivity of the eastern Mediterranean Sea, Global Biogeochem. Cycles, 15, 805–817, 2001.
Lafon, S., Alfaro, S. C., Chevaillier, S., and Rajot, J. L.: A new generator for mineral dust aerosol production from soil samples in the laboratory: GAMEL, Aeolian Res., 15, 319–334, 2014.
Lambert, G. and Nezami, M.: Importance des retombées sèches dans le bilan du plomb-210, Ann. Geophys., 21, 245–251, 1965, http://www.ann-geophys.net/21/245/1965/.
Leong, K. H., Beard, K. V., and Ochs III, H. T.: Laboratory measurements of particle capture by evaporating cloud drops, J. Atmos. Sci., 39, 1130–1140, 1982.
López-García, P., Gelado-Caballero, M. D., Santana-Castellano, D., Suárez de Tangil, M., Collado-Sánchez, C., and Hernández-Brito, J. J.: A three-year time-series of dust deposition flux measurements in Gran Canaria, Spain: a comparison of wet and dry surface deposition samplers, Atmos. Environ., 79, 689–694, 2013.
Losno, R.: Chimie d'éléments minéraux en trace dans les pluies Méditerranéennes, PhD thesis, Université Paris, Paris, 184 pp., 1989.
Loÿe-Pilot, M. D. and Martin, J. M.: Saharan dust input to the Western Mediterranean: an eleven years record in Corsica, in: The Impact of Desert Dust Across the Mediterranean, edited by: Guerzoni, S. and Chester, R., Kluwer Acad. Publ., Dordrecht, 191–199, 1996.
Markaki, Z., Loÿe-Pilot, M. D., Violaki, K., Benyahya, L., and Mihalopoulos, N.: Variability of atmospheric deposition of dissolved nitrogen and phosphorus in the Mediterranean and possible link to the anomalous seawater N/P ratio, Mar. Chem., 120, 187–194, 2010.
Morales-Baquero, R., Pulido-Villena, E., and Reche, I.: Chemical signature of Saharan dust on dry and wet atmospheric deposition in the south-western Mediterranean region, Tellus B, 65, 18720, doi:10.3402/tellusb.v65i0.18720, 2013.
Orange, D., Gac, J. Y., Probst, J. L., and Tanre, D.: Mesure du dépôt au sol des aérosols désertiques. Une méthode simple de prélèvement: le capteur pyramidal, CR Acad. Sci. Paris, 311, 167–172, 1990.

AMTD
8, 2299–2329, 2015

Osada, K., Ura, S., Kagawa, M., Mikami, M., Tanaka, T. Y., Matoba, S., Aoki, K., Shinoda, M., Kurosaki, Y., Hayashi, M., Shimizu, A., and Uematsu, M.: Wet and dry deposition of mineral dust particles in Japan: factors related to temporal variation and spatial distribution, Atmos. Chem. Phys., 14, 1107–1121, doi:10.5194/acp-14-1107-2014, 2014.

Ozsoy, T.: Atmospheric wet deposition of soluble macro-nutrients in the Cilician Basin, north-eastern Mediterranean sea, J. Environ. Monitor., 5, 971–976, 2003.

Pey, J., Querol, X., Alastuey, A., Forastiere, F., and Stafoggia, M.: African dust outbreaks over the Mediterranean Basin during 2001–2011: PM_{10} concentrations, phenomenology and trends, and its relation with synoptic and mesoscale meteorology, Atmos. Chem. Phys., 13, 1395–1410, doi:10.5194/acp-13-1395-2013, 2013.

Pranesha, T. S. and Kamra, A. K.: Scavenging of aerosol particles by large water drops: 1. Neutral case, J. Geophys. Res., 101, 23373–23380, doi:10.1029/96JD01311, 1996.

Prospero, J. M., Landing, W. M., and Schulz, M.: African dust deposition to Florida: temporal and spatial variability and comparisons to models, J. Geophys. Res., 115, D13304, doi:10.1029/2009JD012773, 2010.

Pulido-Villena, E., Wagener, T., and Guieu, C.: Bacterial response to dust pulses in the western Mediterranean: implications for carbon cycling in the oligotrophic ocean, Global Biogeochem. Cycles, 22, GB1020, doi:10.1029/2007GB003091, 2008.

Rajot, J. L.: Wind-blown sediment mass budget of Sahelian village land units in Niger, B. Soc. Geol. Fr., 172, 523–531, 2001.

Remoudaki, E., Bergametti, G., and Buat-Ménard, P.: Temporal variability of atmospheric lead concentrations and fluxes over the Northwestern Mediterranean Sea, J. Geophys. Res., 96, 1043–1055, 1991.

Ridame, C., Guieu, C., and Loÿe-Pilot, M. D.: Trend in total atmospheric deposition fluxes of aluminium, iron, and trace metals in the northwestern Mediterranean over the past decade (1985–1997), J. Geophys. Res., 104, 30127–30138, doi:10.1029/1999JD900747, 1999.

Rognon, P., Coudé-Gaussen, G., Revel, M., Grousset, F. E., and Pedemay, P.: Holocene saharan dust deposition on the Cape Verde Islands: sedimentological and Nd-Sr isotopic evidence, Sedimentology, 43, 359–366, 1996.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, J. Wiley, New York, 136 pp., 1998.

Slinn, W. G. N.: Precipitation scavenging, in: Atmospheric Sciences and Power Production, chapter 11, edited by: Randerson, D., 466–532, no. DOE/TIC-27601 (DE84005177), Office

AMTD
8, 2299–2329, 2015

of Health and Environmental Research, Division of Biomedical Environmental Research, US Dept. of Energy, Washington, D.C., 1984.
Slinn, S. A. and Slinn, W. G. N.: Predictions for particle deposition on natural waters, Atmos. Environ., 14, 1013–1016, 1980.
Sow, M., Goossens, D., and Rajot, J. L.: Calibration of the MDCO dust collector and of four versions of the inverted frisbee dust deposition sampler, Geomorphology, 82, 360–375, 2006.
Sun, H., Nelson, M., Chen, F., and Husch, J.: Soil mineral structural water loss during loss on ignition analyses, Can. J. Soil Sci., 89, 603–610, 2009.
Ternon, E., Guieu, C., Loÿe-Pilot, M.-D., Leblond, N., Bosc, E., Gasser, B., Miquel, J.-C., and Martín, J.: The impact of Saharan dust on the particulate export in the water column of the North Western Mediterranean Sea, Biogeosciences, 7, 809–826, doi:10.5194/bg-7-809-2010, 2010.
Textor, C., Schulz, M., Guibert, S., Kinne, S., Balkanski, Y., Bauer, S., Berntsen, T., Berglen, T., Boucher, O., Chin, M., Dentener, F., Diehl, T., Easter, R., Feichter, H., Fillmore, D., Ghan, S., Ginoux, P., Gong, S., Grini, A., Hendricks, J., Horowitz, L., Huang, P., Isaksen, I., Iversen, I., Kloster, S., Koch, D., Kirkevåg, A., Kristjansson, J. E., Krol, M., Lauer, A., Lamarque, J. F., Liu, X., Montanaro, V., Myhre, G., Penner, J., Pitari, G., Reddy, S., Seland, Ø., Stier, P., Takemura, T., and Tie, X.: Analysis and quantification of the diversities of aerosol life cycles within AeroCom, Atmos. Chem. Phys., 6, 1777–1813, doi:10.5194/acp-6-1777-2006, 2006.
Theodosi, C., Markaki, Z., and Mihalopoulos, N.: Iron speciation, solubility and temporal variability in wet and dry deposition in the Eastern Mediterranean, Mar. Chem., 120, 100–107, 2010.
Venkatram, A. and Pleim, J.: The electrical analogy does not apply to modeling dry deposition of particles, Atmos. Environ., 33, 3075–3076, 1999.
Wang, P. K. and Pruppacher, H. R.: An experimental determination of the efficiency with which aerosol particles are collected by water drops in subsaturated air, J. Atmos. Sci., 34, 1664–1669, 1977.
Wesely, M. L.: Parameterizations of surface resistance to gaseous dry deposition in regional-scale numerical models, Atmos. Environ., 23, 1293–1304, 1989.
Wiggs, G. F. S., Leys, J., McTainsh, G. H., Heidenrich, S., and Strong, C.: A wind tunnel study of the collection efficiency of an aerodynamically improved “Frisbee” dust trap, Proc. ICAR5/GCTE-SEN Joint Conference, 22–25 July 2002, Int. Center for Arid and Semiarid Land Studies, Texas Tech University, Lubbock, Texas, USA, Publ. 02-2, 133–141, 2002.

AMTD
8, 2299–2329, 2015

Zhao, T. L., Gong, S. L., Zhang, X. Y., and McKendry, I. G.: Modeled size-segregated wet and dry deposition budgets of soil dust aerosol during ACE – Asia 2001: implications for trans-Pacific transport, J. Geophys. Res., 108, 8665, doi:10.1029/2002JD003363, 2003.

AMTD
8, 2299–2329, 2015

Table 1. Flow times to drain 100 mL water using various filter membranes.

Filter	AOX 0.4 µm	Nylon 0.45 µm	Cellulose nitrate 0.8 µm	Cellulose ester 0.8 µm	Quartz 2.2 µm
Flow time (min)	67	55	12	5	15

AMTD
8, 2299–2329, 2015

Table 2. Masses of the finest mineral soil fraction (Douz in Tunisia, and Cape Verde in Senegal) deposited on filters and measured before and after ignition at 350, 550 and 950 °C.

Sample	Deposit (g)	Filter + deposit (g) no ignition	Filter + deposit (g) 350 °C ignition	Filter + deposit (g) 550 °C ignition	Filter + deposit (g) 950 °C ignition
Douz 1	0.126	0.215	0.131	0.122	0.113
Douz 2	0.134	0.217	0.137	0.128	0.119
Douz 3	0.257	0.337	0.260	0.251	0.240
Cape Verde 1	0.012	0.095	0.018	0.011	0.012
Cape Verde 2	0.012	0.098	0.015	0.011	0.012
Cape Verde 3	0.015	0.100	0.020	0.013	0.015

AMTD
8, 2299–2329, 2015

Table 3. Masses collected on filters on Frioul Island before and after ignition at 350, 550 and 950 °C.

Sample	Deposit (g)	Filter + deposit (g) no ignition	Filter + deposit (g) 350 °C ignition	Filter + deposit (g) 550 °C ignition	Filter + deposit (g) 950 °C ignition
Filter F7	0.011	0.089	0.017	0.009	0.009
Filter F8	0.091	0.165	0.090	0.082	0.068
Filter F9	0.145	0.221	0.139	0.131	0.106
Filter F10	0.000*	0.076	0.003	0.000	0.001
Filter F11	0.000*	0.075	0.007	0.000	0.001
Filter F12	0.000*	0.077	0.002	0.000	0.001
Filter F13	0.000*	0.077	0.001	0.000	0.000
Filter F14	0.000*	0.078	0.003	0.001	0.001
Filter F15	0.000*	0.078	0.003	0.001	0.000

* In-situ control filter without any deposit.

AMTD
8, 2299–2329, 2015

Table 4. Ignition gradient protocol.

T° range	0–200 °C	200–350 °C	350–550 °C	550 °C
Time	40 min	150 min	45 min	120 min
T° gradient	5 °C min^{-1}	1 °C min^{-1}	4.5 °C min^{-1}	–

AMTD
8, 2299–2329, 2015

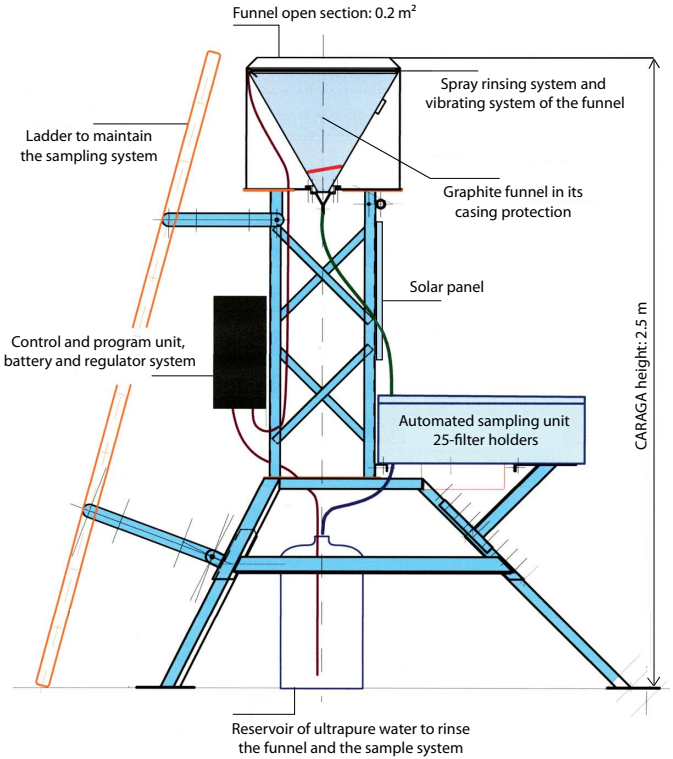

Figure 1. Schema of the CARAGA collector. High of the collector can be extended to one meter more by adding a second pillar spacer.

AMTD
8, 2299–2329, 2015

Figure 2. CARAGA sampling system of total insoluble atmospheric deposition installed on Frioul Island (43.27° N; 5.29° E).

AMTD
8, 2299–2329, 2015

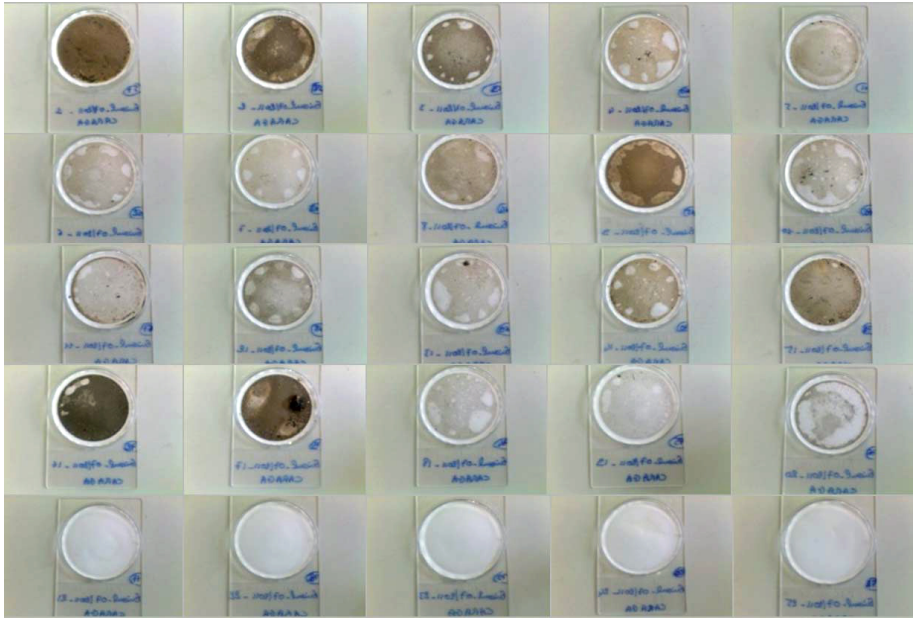

Figure 3. In-situ filters and control blank filters (last filter line) collected at the Frioul site between July and December 2011.

AMTD
8, 2299–2329, 2015

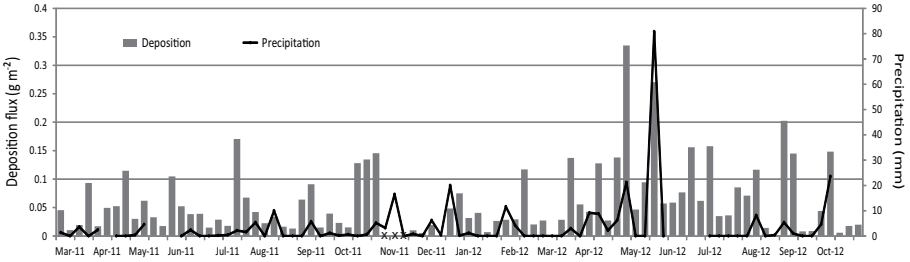

Figure 4. Weekly total insoluble deposition ($g\,m^{-2}$ with an uncertainty of $\pm 5 \times 10^{-3}$ g), and weekly precipitation rate (mm) on Frioul Island from February 2011 to October 2012. The filter was not automatically changed between end of October and mid November 2011. The accumulated deposited flux for this 3 weeks period is $0.26\,g\,m^{-2}$ and is not reported on the figure (black crosses).

AMTD
8, 2299–2329, 2015

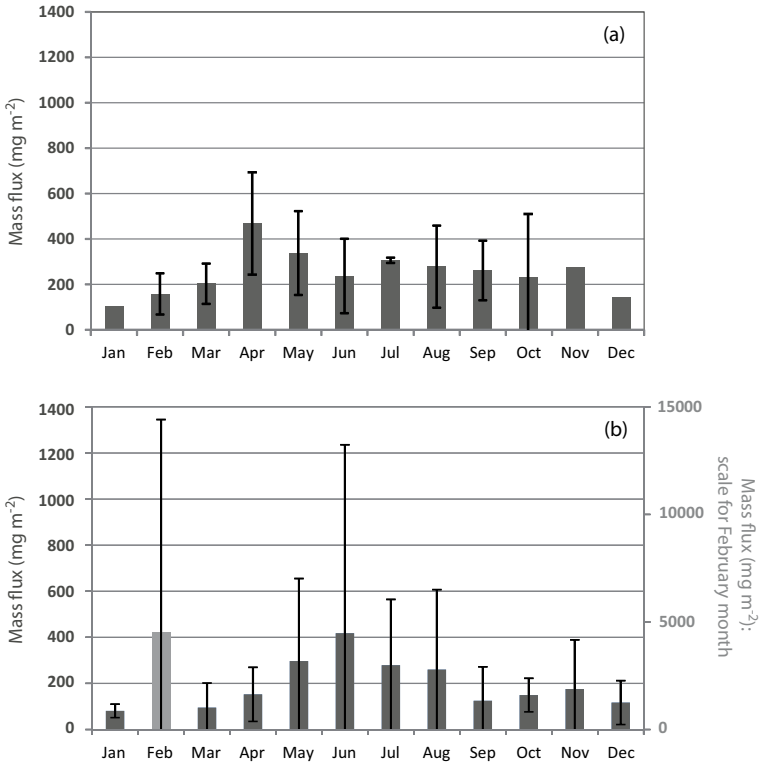

Figure 5. Monthly average insoluble atmospheric deposition in mg m^{-2} **(a)** measured at the Frioul site from February 2011 to October 2012 in the framework of this study, and **(b)** measured in Cap Ferrat and Corsica for 2003–2006 as presented in Ternon et al. (2010) (the scale for February, on the right *y* axis of **(b)**, is different to take into account an extreme Saharan events occurring in February 2004, Ternon et al., 2010). The error bars represent the SD of the mean monthly values.

AMTD
8, 2299–2329, 2015

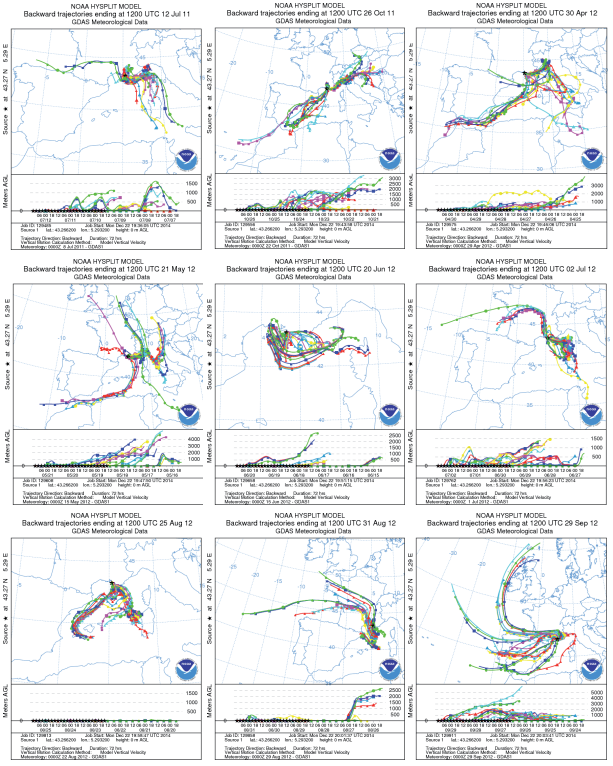

Figure 6. HYSPLIT backward air mass trajectories (starting at 12:00 UTC at ground level, and running for the previous 72 h with a trajectory every 3 h) for the nine main deposition events recorded on Frioul Island between: **(a)** 7 and 14 July 2011, **(b)** 20 and 27 October 2011, **(c)** 26 April and 3 May 2012, **(d)** 17 and 24 May 2012, **(e)** 14 and 21 June 2012, **(f)** 28 June and 5 July 2012, **(g)** 23 and 30 August 2012, **(h)** 30 August and 6 September 2012, and **(i)** 27 September and 4 October 2012.

AMTD
8, 2299–2329, 2015

An automatic collector to monitor insoluble atmospheric deposition

B. Laurent et al.