



Ground level ice nuclei particle measurements including Saharan dust events at a Po Valley rural site (San Pietro Capofiume, Italy)



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ABSTRACT

Filter-collected aerosol samples in the PM₁ and PM₁₀ fractions and particle number concentration were measured during experimental campaigns in a rural area near Bologna (Italy) in the periods 10–21 February 2014 and 19–30 May 2014. Ice nuclei particle (INP) concentrations measured off-line showed prevalently higher average values in the morning with respect to the afternoon, in the PM₁ fraction with respect to PM_{1–10} (with the exception of the first campaign, at $S_w = 1.01$), and at water saturation ratio $S_w = 1.01$ with respect to $S_w = 0.96$.

The aerosol in the coarse size range (1–10 μm) contributed significantly to the total INP concentration. In the first campaign, the average INP concentration in the coarse fraction was 80% of the total in the morning and 74% in the afternoon, at $S_w = 1.01$. In the second campaign, the contribution of the coarse size fraction to the INP number concentration was lower. On the whole, the results showed that the freezing activity of aerosol diameters larger than 1 μm needs to be measured to obtain the entire INP population.

Sahara dust events (SDEs) took place during both campaigns, in the periods 17–20 February and 21–23 May 2014. Results show that the averaged particle number concentration was higher during SDE than during no-Saharan dust events. A low correlation between INP and total aerosol number concentration was generally measured, except for SDEs observed in February, in which the correlation coefficient between aerosol concentration in the coarse fraction and INP in the same range, at water supersaturation, was about 0.8.

Precipitation events influenced the aerosol concentration. In the February campaign, lower values of INP and particle concentrations were measured in case of heavy rain events. During the May campaign, an average number concentration of the aerosol in the range 0.5–10 μm was slightly higher than on days when no precipitation was measured, the rainfall intensity being low. Only in a few cases did we note a sharp drop in INP in the PM₁₀ fraction at $S_w = 1.01$ (26 May, 8 a.m. and 1 p.m.; 27 May, 1 p.m.).

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1. Introduction

Insoluble aerosol particles that catalyze the formation of ice crystals in clouds are called ice nuclei particles (INP) (Vali et al., 2015) and can form ice through four different thermodynamic mechanisms: deposition, condensation-freezing, immersion-freezing, and contact-freezing.

Ice nuclei can be measured with a variety of techniques: mixing chambers (Langer, 1973; Bundke et al., 2008), expansion cloud chambers (Möhler et al., 2003; Tajiri et al., 2013), continuous flow diffusion chambers (Al-Naimi and Saunders, 1985; Rogers et al., 2001), and the filter method (Bigg, 1996; Klein et al., 2010; Langer and Rodgers, 1975). Each device has advantages and disadvantages. For instance, the continuous flow diffusion chamber (CFCD) cannot detect contact-freezing, and aerosol particles larger than about 2 μm need to be removed with an impactor to distinguish ice crystals reliably from background aerosols. In addition, the CFCD provides no information on the

size distribution of INP. Besides cloud chambers and CFCD devices, many droplet-freezing techniques are available for immersion mode ice nucleation (Ardon-Dryer et al., 2011; Budke and Koop, 2015; Knopf and Alpert, 2013; Murray et al., 2011; Vali, 2008).

Membrane filter techniques have been used in different forms for a number of years. Particle sampling on filters can be convenient, because the samples can be processed later without nuclei degradation, and aerosol activation can be measured in all size ranges, and can simulate deposition, condensation and contact nucleation modes (Bigg, 1990a; Cooper, 1980; Stevenson, 1968). The temporal resolution is usually no better than 20–30 min. Early designs used a static vapour diffusion field, but several factors led to an underestimation of the ice nuclei (volume effect, chamber height effect, vapour depletion on the filter around growing crystals and hygroscopic particles, vapour competition between ice nuclei). However, Bigg (1990a) concluded that with suitable precautions the filter method is adequate for INP measurements. In order to circumvent some of the problems arising with the static chamber, a dynamic chamber filter processing chamber (DFPC) was introduced (Langer and Rodgers, 1975).

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CFDC measurements sometimes yielded INP higher concentrations than the filter method (Al-Naimi and Saunders, 1985; Hussain and Saunders, 1984). In simultaneous comparison, Hussain and Kayani (1988) found that at water saturation their CFDC detected fourteen times as many nuclei than filters processed in a static chamber. However, in a similar comparison Saunders and Al-Juboory (1988) found nearly equivalent results between a CFDC and DFPC filters at $-16\text{ }^{\circ}\text{C}$ and supersaturation with respect to water between -3% and $+5\%$.

Plaude et al. (1996) performed simultaneous measurements on INP concentration using a cloud chamber and a filter technique on the territory of the former USSR over a five-year period. The agreement between the results obtained by the two techniques was found to depend on the overall pollution of the region, and is higher in a relatively clean atmosphere ($\text{INP}_{\text{chamber}}/\text{INP}_{\text{filter}} \sim 1.9$), and lower in an urban area which is more polluted ($\text{INP}_{\text{chamber}}/\text{INP}_{\text{filter}}$ in the range 4 to 7).

Most INP measurements concern total INP number concentrations with less emphasis on determining their size distribution. In point of fact, information on airborne INP size distribution may be helpful to identify the predominant INP sources. For instance, primary biological aerosol particles can span physical dimensions of a few nanometers to hundred of micrometers (Huffman et al., 2012), whereas black carbon particles are mainly in the submicron range (Clarke et al., 2004; Schwarz et al., 2008). Therefore, size-resolved measurements of ice nucleating particles should be performed and even super-micron particles should be considered. Previous field size-resolved INP measurements are scarce (Berezinski et al., 1988; Huffman et al., 2013; Rosinski et al., 1986, 1988; Santachiara et al., 2010).

Mason et al. (2016) recently attempted to tackle this problem using a technique which combines aerosol particle collection by a cascade inertial impactor (Moudi MSP Corp., USA) and a microscope-based immersion-freezing apparatus. The results showed that coarse aerosol particles are a significant component of the ice nuclei population in many different ground-level environments (see Tables 2a and 2b of the paper).

Our paper reports the results of two experimental campaigns performed with the filter method at a rural background site. This procedure activates all size ranges of aerosol in the deposition and condensation-freezing modes for the examination of fine and coarse particles. Even if the sampling site is a rural area, it is surrounded by highly populated industrialized regions.

Our measurements were performed at ground level. To date, few INP measurements at ground level in low polluted areas have been reported in the literature. Ground-based INP measurements are important as INP can originate from the surface and be transported to higher levels (Ardon-Dryer et al., 2011; Alizadeh-Choobari et al., 2015; Després et al., 2012; Mamouri and Ansmann, 2015). The aim of the campaigns was to characterize the considered site with respect to certain INP properties, i.e. concentrations, and their relationship with particle number concentration, diurnal variations and possible sources.

2. Experimental

Two experimental campaigns were performed at the “Giorgio Fea” Meteorological Station in San Pietro Capofiume (SPC), a rural site located at about 30 km north-east of Bologna in the eastern Po Valley ($44^{\circ}39'16.33''\text{N}$; $11^{\circ}37'22.28''\text{E}$) in the periods 10–21 February 2014 and 19–30 May 2014. The first campaign was characterized by air masses from the North Atlantic at the beginning of the sampling period, and from Northern Africa in the central part of the campaign, giving rise to Saharan dust episodes (SDEs). In the second campaign air masses came from South Italy during most of the sampling period, and only a short SDE occurred.

PM_1 and PM_{10} aerosol fractions were sampled on nitrocellulose membrane (Millipore HABG04700, nominal porosity $0.45\text{ }\mu\text{m}$) twice a day (8 a.m.–1 p.m., UTC), at 2 m above ground level. The mean flow rate was 38.3 lpm (Bravo H Plus, TCR Tecora) with a sampling time of 15 min. Aerosol fractions were sampled by inserting different sampling

heads ($1\text{ }\mu\text{m}$, and $10\text{ }\mu\text{m}$ cut-point-Standard EN 12341, TCR Tecora) in front of the filter. Particle number concentration in different size classes starting from diameter larger than $0.3\text{ }\mu\text{m}$ was measured at the same time (Optical Spectrometer, Mod.1.108, Grimm Aerosol Technik GmbH). Meteorological data (air temperature, wind speed, pressure) were recorded. The data are reported in Tables 1a–2b.

Back-trajectories were calculated through the NOAA HYSPLIT model, while dust model forecast (Nickovic et al., 2001; Pérez et al., 2006) were obtained through BSC-DREAM from the Barcelona Supercomputing Center (BSC). Distribution of dust around the Mediterranean region can be forecast 72 h in advance, and wind profiles can also be observed. INP concentrations were detected by the membrane filter technique (Bigg, 1990b; Bigg et al., 1963; Lala and Jiusto, 1972; Jiusto et al., 1976; Stevenson, 1968) following the procedure shown in Santachiara et al. (2010). Here we summarize the main points. Filters were inserted into a metal plate, previously covered with a smooth surface of vaseline. Subsequently the vaseline was slightly heated and rapidly cooled in order to fill the filter pores. A replica of the Langer dynamic filter processing chamber (DFPC) (Fig. 2 in Santachiara et al., 2010) housed in a refrigerator was used to detect and determine the concentration of aerosol particles active as INP at different supersaturations with respect to ice and water. By controlling the temperatures of the filter and the air, saturated with respect to finely minced ice and flowing continuously grazing the filter, it was possible to obtain different water saturation ratios S_w . Measurements were performed at $T_{\text{filter}} = -18\text{ }^{\circ}\text{C}$, and $S_w = 0.96$ and 1.01 , respectively.

Measurements with the DFPC below water saturation ($S_w < 1$) should represent deposition-nucleation, and above water saturation ($S_w \geq 1$) deposition and condensation-freezing. A much-discussed question concerns the difference between the processes of condensation-freezing (ice forms after the condensation of water onto an INP) and immersion-freezing (ice nucleated on a solid particle immersed in a supercooled droplet). In practice, the distinction between condensation-freezing and immersion-freezing is not always clear (Dymarska et al., 2006). The results of Wex et al. (2014) and Hiranuma et al. (2015) support the hypothesis that condensation and immersion-freezing might basically be the same process.

3. Results and discussion

Table 1a shows meteorological data, INP and particle number concentrations for each sampling day of the first campaign, while the INP averaged value and the INP ratio between PM_1 and PM_{10} are given in Table 1b. The data of the second campaign are shown in Tables 2a and 2b.

In a few cases, the INP concentration in PM_1 fraction, reported in the above cited Tables, is higher than the corresponding PM_{10} concentration. It is known that INP measurements performed by off-line methods include a complex procedure (sampling of air on filter, preparation of filters and detection of INP, as described in the paper) and that the technique holds intrinsic uncertainty. Repeated analysis of simultaneously sampled filter can yield some spread in the number of observed INPs (Schrod et al., 2016). Furthermore, it is an open question if repeated deposition/condensation experiments at the same temperature and water vapour saturation ratio gives the same results (Knopf and Koop, 2006; Wang and Knopf, 2011; Wang et al., 2012).

Given these reasons, we have decided to provide all the results obtained from the measurements, avoiding manipulations of the datasets, to give a measure of the uncertainty associated to the presented observations. In any case, these uncertainties do not invalidate the obtained results and the conclusions derived from them.

Figs. 1 and 2 show the time series of INP concentrations in the PM_1 and PM_{10} fractions at both saturation ratios ($S_w = 0.96$ and $S_w = 1.01$) during samplings in the morning and in the afternoon. The particle number concentration, obtained from the optical particle counter, in

Table 1a

Meteorological data, particles and INP concentrations during the February 2014 campaign.

Date	Time UTC	T (°C)	R.H. (%)	Wind dir. deg.	Wind vel. (m s ⁻¹)	Part. conc. >0.5 μm (m ⁻³)	INP PM ₁ S _w 0.96 (m ⁻³)	INP PM ₁₀ S _w 0.96 (m ⁻³)	INP PM ₁ S _w 1.01 (m ⁻³)	INP PM ₁₀ S _w 1.01 (m ⁻³)
10/02	8 am	8.4	72.7	99	4.2	7.05 10 ⁶	27.6	13.6	55.1	160.7
	1 pm	8.4	84.8	63	5.8	4.97 10 ⁶	2.8	24.5	19.5	130.9
11/02	8 am	6.3	87.0	268	2.4	4.60 10 ⁶	20.0	5.5	85.7	276.9
	1 pm	8.9	74.1	282	3.0	2.24 10 ⁶	22.0	54.6	35.7	273.2
12/02	8 am	8.2	79.8	295	5.7	3.04 10 ⁶	11.0	30.4	88.1	430.8
	1 pm	11.0	66.0	292	4.7	1.38 10 ⁷	25.0	38.5	105.6	283.5
13/03	8 am	5.9	73.0	269	0.8	7.54 10 ⁶	57.0	89.5	81.1	477.6
	1 pm	9.9	76.8	44	3.8	8.05 10 ⁶	26.2	37.2	55.3	151.8
14/02	8 am	6.3	76.8	288	4.9	1.28 10 ⁷	40.0	35.4	165.5	128.0
	1 pm	13.0	50.0	104	1.2	5.11 10 ⁶	31.1	47.4	36.7	209.2
17/02	8 am	9.1	87.4	300	2.9	3.86 10 ⁷	42.8	54.3	82.7	176.6
	1 pm	11.0	80.0	329	2.3	3.57 10 ⁷	39.2	111.1	84.0	283.3
18/02	8 am	6.7	94.1	120	0.3	8.16 10 ⁶	38.3	45.4	76.5	230.0
	1 pm	11.0	74.3	48	2.0	7.96 10 ⁶	42.0	100.0	80.8	382.2
19/02	8 am	9.0	91.5	319	2.5	6.93 10 ⁷	28.6	73.0	68.6	752.2
	1 pm	11.0	83.1	127	1.3	3.94 10 ⁷	73.2	55.8	81.6	94.8
20/02	8 am	9.0	93.3	353	1.8	4.06 10 ⁶	8.4	13.6	22.3	231.1
	1 pm	9.0	89.5	18	3.6	2.47 10 ⁶	27.9	13.9	44.6	133.3
21/02	8 am	9.7	84	275	4.1	1.24 10 ⁷	76.9	82.3	74.0	908.3
	1 pm	13.3	62	310	2.4	1.10 10 ⁷	54.1	70.9	75.2	478.7

the size ranges 0.5–1 μm and larger than 1 μm (hereafter called coarse fraction), are also given.

By examining the data reported above, we note prevalently higher average INP concentrations in the morning with respect to the afternoon, in the PM₁ fraction with respect to PM_{1–10} (with the exception of the first campaign, at S_w = 1.01) and at water super-saturation with respect to water sub-saturation.

The higher average INP concentrations observed in the morning with respect to the afternoon are likely due to the prevalently higher aerosol concentration in the morning, related to the lower height of the boundary layer, as suggested also by particle number concentration (Figs. 1 and 2).

In the first campaign, the aerosol in the size range 1–10 μm contributed significantly to the total INP concentration: in the morning 28% at S_w = 0.96, and 80% at S_w = 1.01. In the afternoon, the contribution was 38% and 74%, respectively. The average INP concentrations in the PM₁ and PM₁₀ fractions at S_w = 1.01 were 69 and 310 m⁻³, respectively. In the second campaign, the contribution of the coarse size fraction (1–10 μm) to the INP number concentration was lower, at S_w = 1.01. The average INP concentrations in the PM₁ and PM₁₀ fractions at S_w = 1.01 were 107 and 171 m⁻³, respectively.

In a previous campaign, performed in the period 09–12 July 2007, at S_w = 1.00 and T_{filter} = -19 °C, the ratio between INP_{PM1}/INP_{PM10} was 59%, and the ratio between INP in the PM₁ and in the total suspended particles was 49% (Santachiara et al., 2010). The average INP concentrations in the PM₁ and PM₁₀ fractions were 101 m⁻³ and 171 m⁻³, respectively. Therefore, the concentrations are comparable to values measured in the May 2014 campaign, in similar activation conditions. On the whole, the results show that the freezing activity of aerosol diameters larger than 1 μm need to be measured to obtain the entire INP population, in agreement with the recent findings of Mason et al. (2016). In both campaigns the increase in INP in the PM₁ fraction was mostly scant by operating below and above water saturation. We note, for instance, that smaller mineral dust particles prevalently

require water supersaturation to be activated at T = -18 °C (Welti et al., 2009).

Comparison of INP with total particle concentration (with diameter larger than 0.5 μm) yields nucleating fractions of the order of 10⁻⁵–10⁻⁶ INP per particle.

Regarding the anomaly of the INP_{PM1}/INP_{PM10} ration in the first campaign at S_w = 1.01, measurements showed that it is due to both reduced nucleation efficiency of sub-micrometer particles in February with respect to May, at S_w = 1.01, and to enhanced nucleation observed for coarse particles.

High contribution from biomass burning sources (domestic heating) is well documented for winter months in the Po Valley (Gilardoni et al., 2011, 2014; Larsen et al., 2012; Paglione et al., 2014; Perrino et al., 2014; Sandrini et al., 2014; Pietrogrande et al., 2015, 2016). Said contribution is virtually absent in warmer months (Decesari et al., 2014; Rinaldi et al., 2015). Hoose and Moehler (2012) in their review concluded that soot is a generally worse ice nucleus than mineral dust. Same conclusions were obtained by Levin et al. (2016), in their study on ice-nucleating properties of biomass emissions. Therefore, the reduced nucleation activity of PM₁ particles can be reasonably attributed to the enhance contribution of carbonaceous particles from biomass burning, characterizing the site during winter.

On the other hand, the higher activation of super-micrometer particles observed in February suggests different nucleating properties for the coarse aerosol populations in the two campaigns. Unfortunately, the lack of chemical/mineralogical composition data does not allow testing this hypothesis.

3.1. Saharan dust events

During both campaigns Sahara dust events (SDEs) took place, easily recognizable by “red rain” if wet deposition occurs. In this case, the aerosol scavenged from droplets in cloud and below cloud does not contribute to ice nucleation, as droplets are not sampled on filters. Several

Table 1bAveraged INP concentration in the PM₁ and PM₁₀ size fractions of the first campaign (February 2014).

S _w		INP PM ₁ (m ⁻³)	INP PM ₁₀ (m ⁻³)	INP _{PM1} /INP _{PM10} %	INP _{PM1} /(INP _{PM10} - INP _{PM1})
S _w = 0.96	Morning	35.1 (8.4–76.9)	48.5 (89.5–5.5)	72	2.62
	Afternoon	34.4 (73.2–2.8)	55.8 (111.1–13.9)	62	1.61
S _w = 1.01	Morning	75.8 (165.5–13.6)	377.2 (908.3–128.0)	20	0.25
	Afternoon	61.9 (105.6–19.5)	242.1 (478.7–94.8)	26	0.34

Table 2a

Meteorological data, particles and INP concentrations during the May 2014 campaign.

Date	Time UTC	T (°C)	R.H. (%)	Wind dir. deg.	Wind vel. (m s ⁻¹)	Part. conc. >0.5 μm (m ⁻³)	INP PM ₁ S _w 0.96 (m ⁻³)	INP PM ₁₀ S _w 0.96 (m ⁻³)	INP PM ₁ S _w 1.01 (m ⁻³)	INP PM ₁₀ S _w 1.01 (m ⁻³)
19/05	8 am	17.2	67.7	284	2.9	7.41 10 ⁶	91.0	92.6	151.7	77.1
	1 pm	22.1	36.6	194	6.6	2.71 10 ⁶	50.2	157.0	62.8	109.9
20/05	8 am	19.0	67.4	192	6.1	1.07 10 ⁷	93.8	46.9	78.2	172.0
	1 pm	23.9	38.6	194	6.6	4.25 10 ⁶	97.3	158.4	113.5	190.1
21/05	8 am	23.2	52.3	288	4.1	9.08 10 ⁶	65.1	47.5	178.9	183.7
	1 pm	25.5	44.6	223	7.2	3.19 10 ⁶	78.9	92.8	63.1	160.8
22/05	8 am	22.7	59.2	315	5.3	6.57 10 ⁶	191.6	251.8	239.5	252.0
	1 pm	27.0	42.5	322	5.6	8.00 10 ⁶	71.4	110.6	48.7	142.2
23/05	8 am	21.7	59.1	325	4.3	1.37 10 ⁷	63.5	100.5	104.8	172.7
	1 pm	25.5	46.2	46	2.8	2.41 10 ⁶	80.9	93.4	161.7	327.0
26/05	8 am	19.3	74.6	269	4.0	3.34 10 ⁶	30.9	9.1	40.2	97.3
	1 pm	21.1	66.7	306	5.9	3.78 10 ⁶	119.3	97.3	157.0	108.3
27/05	8 am	18.5	59.7	270	3.9	2.32 10 ⁶	90.3	102.8	124.6	155.7
	1 pm	22.1	45.2	180	6.2	2.05 10 ⁶	62.2	47.1	93.4	84.8
28/05	8 am	19.9	52.9	170	5.5	2.58 10 ⁶	30.9	94.0	92.7	282.1
	1 pm	19.6	62.9	184	3.8	1.47 10 ⁶	101.9	95.1	147.9	206.2
29/05	8 am	18.1	62.9	129	2.5	2.96 10 ⁶	47.8	108.3	44.6	278.6
	1 pm	22.7	45.8	128	3.5	5.86 10 ⁶	79.3	108.2	95.1	197.8
30/05	8 am	20.7	58.9	269	3.2	5.89 10 ⁶	22.1	63.5	63.3	66.6
	1 pm	25.5	40.6	233	3.7	7.87 10 ⁶	16.1	152.5	96.7	165.2

procedures can be used to recognize SDEs and characterize dust source areas, e.g. remote sensing, inversion of the wavelength dependence of the single scattering albedo, chemical and differences in dust particles reaching sampling stations (Coen et al., 2004; Goudie and Middleton, 2001).

We examined the four-day backward trajectories, the forecast of the dust load over Northern Africa and Europe, and of dust load deposition, finding SDEs in the period 17–20 February (first campaign) and 21–23 May (second campaign). Figs. 3–4 show the dust load over Northern Africa and Europe and back-trajectories arriving at SPC at 500 m above ground level (AGL) on 18 and 19 February, respectively. Figs. 5–6 show dust-load and back-trajectories on 22 and 23 May.

The effect of dust transport from major desert regions on aerosol composition and deposition are known to extend globally (Husar et al., 2001; Prospero, 1996, 1999). Saharan dust is generally mobilized in Libya, Egypt and the Bodele Depression and then transported over the Mediterranean by a combination of low and high pressure systems.

Mineral dust has been recognized as the most important INP in the atmosphere (Kamphus et al., 2010). In case of mineral dust aerosol originated from desert regions like the Sahara and the Gobi, the particles are lifted into the free troposphere during storm events. Particles are subsequently transported over long distances (DeMott et al., 2003; Prodi and Fea, 1979; Prospero, 1999; Sassen et al., 2003) and undergo aging processes as a result of condensation of low or semi-volatile compounds on the particle surface. Levin et al. (1996) observed that mineral dust is often coated with sulphate and other soluble materials. Such additions may influence the efficiency of mineral dust to act as ice nuclei (Möhler et al., 2005, 2008; Sullivan et al., 2010). Niedermeier et al. (2010) found that active sites were lost when particles were processed with concentrated sulphuric acid. In laboratory experiments they showed that the ice nucleation ability of (NH₄)₂SO₄-coated particles is reduced by one order of magnitude in terms of the determined ice

fractions compared to uncoated particles, in the range –40 to –30 °C. Soluble coatings deposited on atmospheric particles during transport can alter and reduce their nucleating ability (Archuleta et al., 2005; Bertram et al., 2000; Zuberi et al., 2002). Eastwood et al. (2009), and Kulkarni et al. (2014) measured a lower nucleation efficiency for kaolinite coated with sulphuric acid with respect to the bare mineral. The chemical aging of the dust particles can even affect water uptake and the activation of cloud condensation nuclei and hence rain formation. Therefore, it is unlikely that mineral dust is found in its pure, untreated form after a few hours or days of residence time in the atmosphere.

Table 3 shows the particle number and INP concentrations during SDEs and during no-Sahara dust events (NSDEs) for both campaigns.

The averaged particle number concentration is higher during SDEs than during NSDEs. The average INP concentration in the SDEs and NSDEs are comparable in the PM₁ and in the PM₁₀ fractions (S_w = 1.01) for the February campaign, while in the second campaign the INP concentration in the PM₁₀ fraction is higher during SDEs. It is important to note that the measured and sampled aerosol can include both local sources and mineral dust transport from desert regions.

The origin of the air mass, in each sampling period, were analyzed through NOAA HYSPLIT model and classified into different provenance directions: from North Atlantic, Sahara Dust Events and from North East with a circulation over the Adriatic sea. The averaged INP activation fractions in each direction was computed for the coarse fraction (PM_{1–10}). The obtained activation fractions values, for each direction, were of 7.1 · 10⁻⁴, 1.8 · 10⁻⁴ and 3.0 · 10⁻⁴, respectively. Therefore during Sahara Dust Events, particles belonging to the coarse fraction were less active as ice nuclei with respect to other directions.

In the afternoon of the 17 and 18 February, and in the morning of 19 there was a relatively high INP concentration in the PM₁₀ fraction (S_w = 1.01) and a high concentration of aerosol in the coarse range. However, lower activation fractions were measured during the 17 and

Table 2bAveraged INP concentration in the PM₁ and PM₁₀ size fractions of the second campaign (May 2014).

S _w		INP PM ₁ (m ⁻³)	INP PM ₁₀ (m ⁻³)	INP _{PM1} /INP _{PM10} %	INP _{PM1} /(INP _{PM10} -INP _{PM1})
S _w = 0.96	Morning	72.7 (191.6–22.1)	91.7 (251.8–9.1)	79	3.83
	Afternoon	67.8 (101.9–16.1)	111.2 (158.4–47.1)	61	1.56
S _w = 1.01	Morning	111.2 (239.5–31.4)	166.2 (282.1–21.7)	67	2.02
	Afternoon	97.7 (161.7–48.7)	162.4 (327.0–40.2)	60	1.51

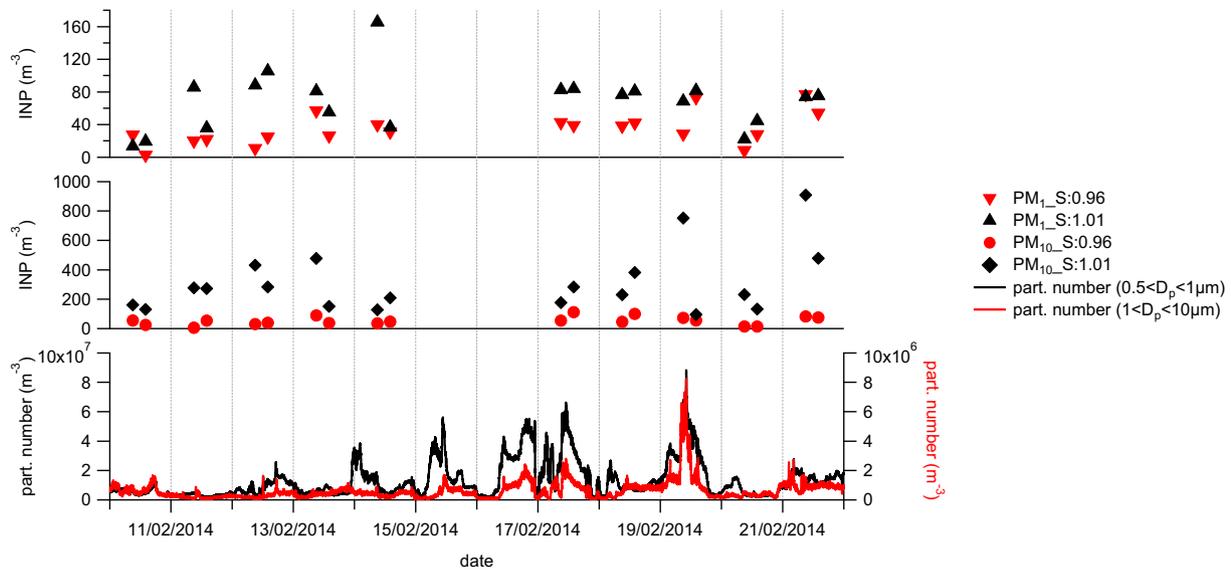


Fig. 1. INP and particle number concentrations (February 2014).

19 February, days affected by SD transport events. Lower INP concentrations in the afternoon of 20 February can be due to an almost continuous rain precipitation.

Concerning 19 February, the highest aerosol concentration of the campaign was measured both in the fine and coarse fraction, being lower in the afternoon with respect to the morning. In the morning the contribution of the coarse fraction is prevalent, and the INP concentration is high ($\approx 750 \text{ m}^{-3}$ in the PM_{10} fraction at $S_w = 1.01$), whereas in the afternoon the INP concentration was low and comparable both in the fine and coarse fraction at $S_w = 0.96$ and 1.01.

Back-trajectories at 500 m AGL do not show meaningful variations in the afternoon with respect to morning. Only surface wind changes from NW (polluted area) in the morning to SE in the afternoon (Adriatic Sea). In the afternoon there were rain events. As sampling is performed in a rural area, we cannot rule out an increase in ammonia concentration due anthropogenic activities for agricultural operations, as NH_3 decreases the ice nucleation ability of the aerosol (Birstein, 1960).

3.2. INP and aerosol particle concentration

The correlation between INP and number aerosol concentration is an open question. A parameterization linking INP number concentrations active at water saturation or above, and the aerosol number concentration exceeding $0.5 \mu\text{m}$ diameter was suggested by DeMott et al. (2011). Prevalently, a correlation was found between INP number concentrations and number concentrations of the total aerosol particles larger than $0.5 \mu\text{m}$ (Jiang et al., 2015; Mason et al., 2015; Schwikowski et al., 1995).

During a dust event, Chou et al. (2011) found a possible correlation between the INP number concentration and the increase in larger particles. Schwikowski et al. (1995) showed that the concentration of larger particles increased during the considered dust event, accompanied by a depletion in the ultrafine particle concentration. In some cases, no correlation was found (Rogers et al., 1998). Richardson et al. (2007) observed an increase in particle concentration in the accumulation mode,

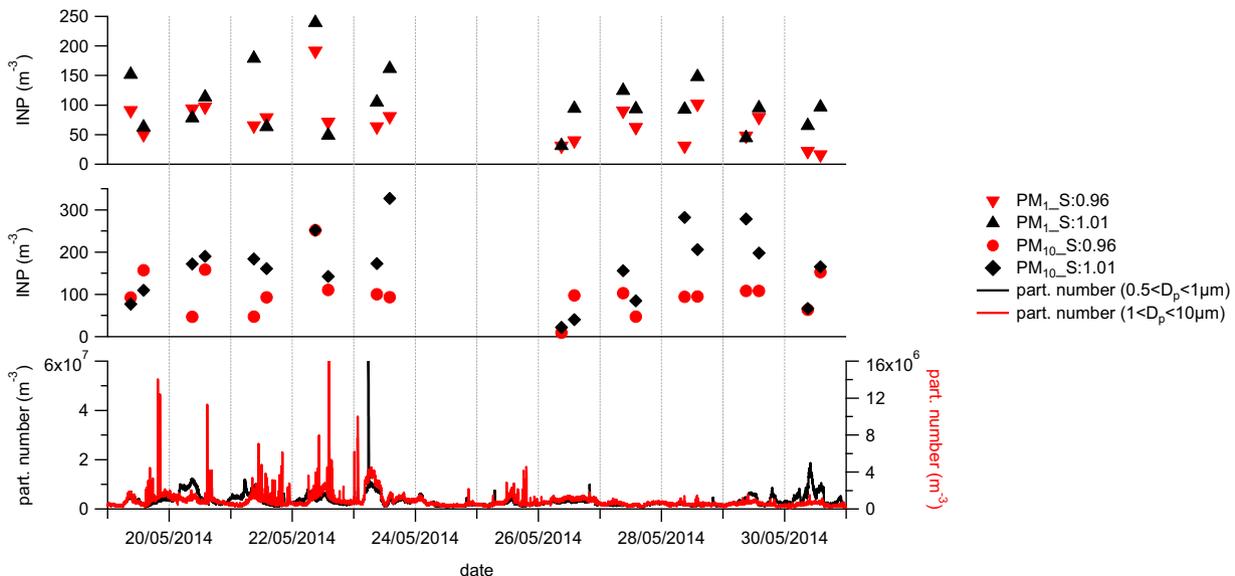


Fig. 2. INP and particle number concentrations (May 2014).

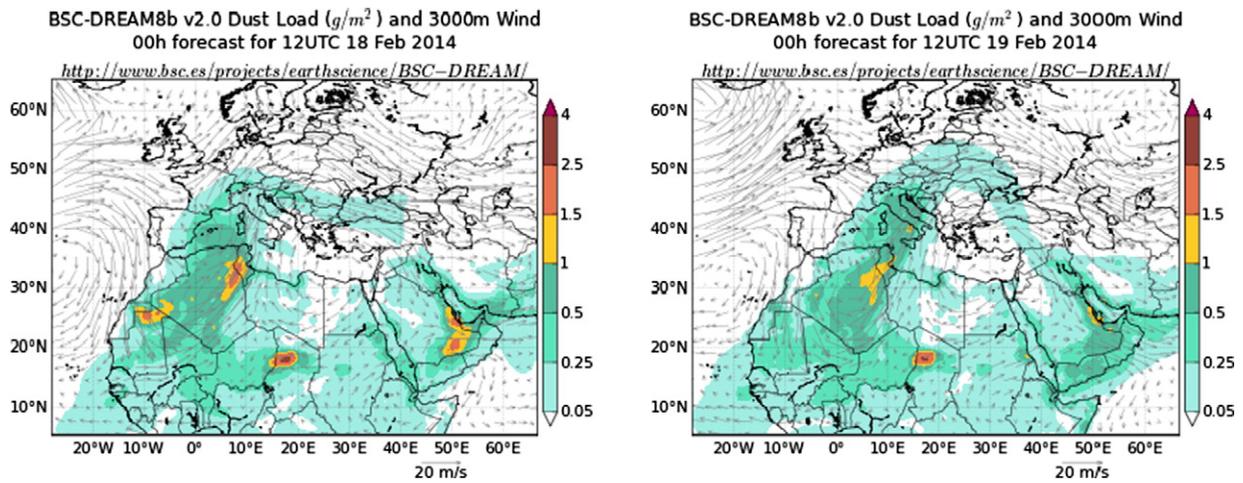


Fig. 3. Dust load distribution over the Mediterranean region on 18 and 19 February 2014 at 12 a.m. UTC.

not matched by an increase in INP. It was suggested that these particles were either poor INP or pollutants had a negative effect on INP.

In our campaign, a low correlation between INP and aerosol total number concentrations was generally observed, except for February SDE, in which the correlation coefficient between aerosol concentration in the coarse fraction and INP in the same range was about 0.8 ($S_w = 1.01$). On the contrary, significant correlation was observed when considering the size segregated particle number concentration, for the February campaign (Fig. 7). Particularly, INP concentration significantly correlated ($p < 0.01$) with particle number in the range 1–10 μm , with maximum correlation in the 3–5 μm size range. A similar profile for the correlation coefficient as a function of the particle size range was observed for the second campaign also, although the correlation cannot be considered statistically significant in this case.

Our data suggest that INP concentration in the PM_{1-10} fraction is mainly driven by 3–5 μm particles in the study area.

The overall low correlation observed depends on the variety of parameters related to ice nucleation processes. Even assuming that the aerosol number concentration is equal in two different events, particles can have different nucleation activity at a fixed temperature and relative humidity depending on: chemical composition (internally or externally mixed, purely soluble, purely insoluble or composed of both insoluble and soluble material), amorphous or crystalline structure matching or not with the ice lattice, and their surface area. Experiments have established that heterogeneous ice nucleation is a very localized phenomenon in that it proceeds at distinct active sites on a substrate surface: cracks, cavities, chemical impurity, and etching (Marcolli, 2014).

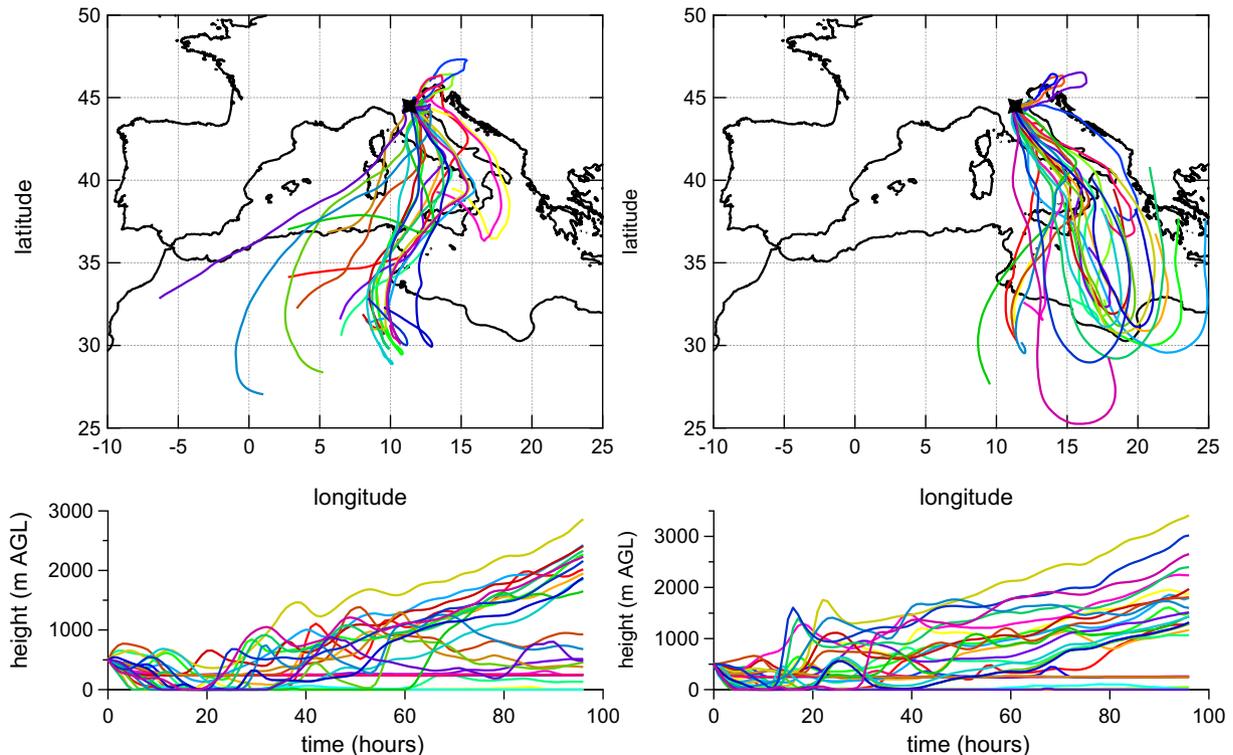


Fig. 4. The 4-day backward trajectories of air masses arriving at SPC at 500 m AGL at 1 p.m. UTC on 18 (left) and 19 February 2014 (right), calculated by the NOAA HYSPLIT model.

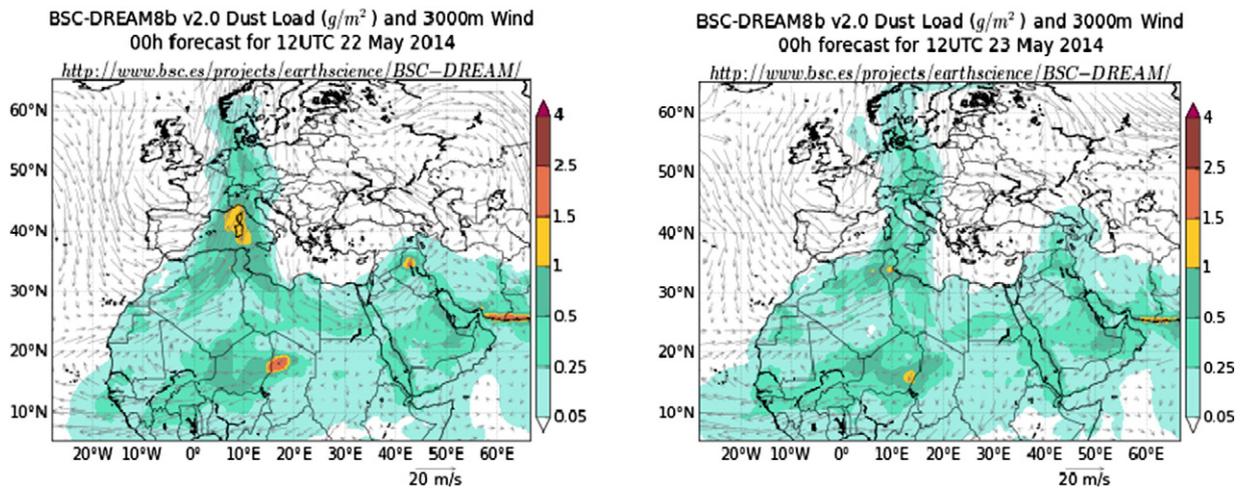


Fig. 5. Dust load distribution over the Mediterranean region on 22 (left) and 23 May 2014 (right) at 12 a.m. UTC.

By considering the data of 17 February and comparing particle concentration in the morning and in the afternoon, we note in both cases a high aerosol concentration with respect to the remaining sampling days. In addition, at time 1 p.m. the concentration in the coarse fraction was higher by about a factor ten with respect to 8 a.m., while concentrations in the 0.5–1 μm size range were comparable. In agreement with these data, INP concentrations in the PM_{10} fraction were comparable in the morning and in the afternoon, while in the $\text{PM}_{2.5}$ fraction the INP concentration was slightly higher in the afternoon, at both $S_w = 0.96$ and $S_w = 1.01$. Backward trajectories arriving at SPC at 8 a.m. and at 1 p.m. UTC show air masses travelling for long periods across the Mediterranean sea: 48 h prior to sampling site the air masses were at low level (~ 500 m AGL), and therefore marine aerosol and mixed soluble/insoluble aerosol should be present. The highest INP concentration was

measured in the morning of 21 February ($\approx 900 \text{ m}^{-3}$), while in the afternoon the INP concentration was lower ($\approx 480 \text{ m}^{-3}$). Back trajectories were from NE both in the morning and in the afternoon, moving slowly inside the continent. Surface winds were from the West in the morning and from NW in the afternoon. The concentration of the coarse particle was high, about $1.32 \cdot 10^6 \text{ m}^{-3}$ in the morning, and $0.91 \cdot 10^6 \text{ m}^{-3}$ in the afternoon. Our experimental data show that air masses that travelled for a long time through sea prevalently show lower values of the activation fraction.

3.3. INP and precipitation

During precipitation events in the February campaign (10 and 20 February) lower values of INP and particle concentrations were

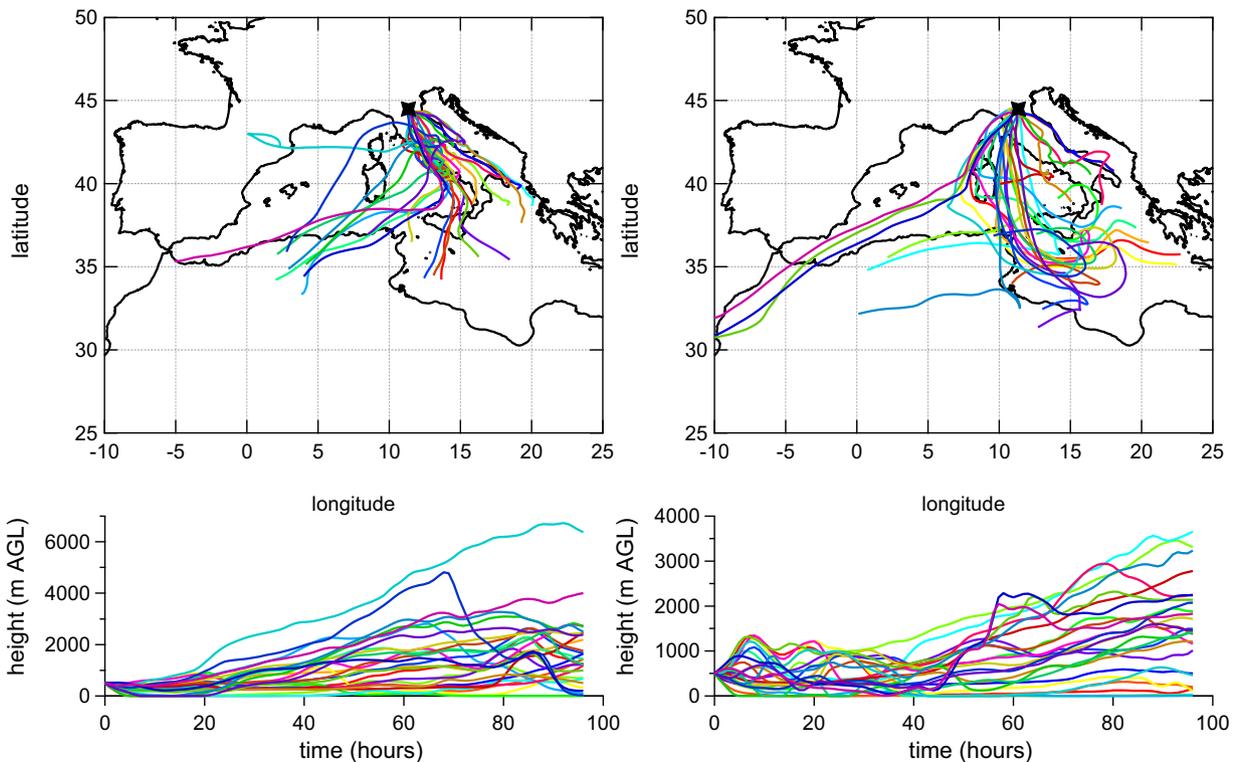


Fig. 6. The 4-day backward trajectories of air masses arriving at SPC at 500 m AGL at 1 p.m. UTC on 22 (left) May and 23 May 2014 (right), calculated by the NOAA HYSPLIT model.

Table 3

Particle number and INP concentrations ($S_w = 1.01$) during SDEs and NSDEs in both campaigns.

		Part. conc. >0.5 μm (m^{-3})	Part. conc. 1–10 μm (m^{-3})	INP PM1 (m^{-3})	INP PM10 (m^{-3})
1st campaign	SD	$2.5 \cdot 10^7$	$1.3 \cdot 10^6$	69.0	367.1
	NSD	$7.6 \cdot 10^6$	$4.7 \cdot 10^5$	69.7	325.8
	SD/NSD	3.3	2.6	1.0	1.1
2nd campaign	SD	$7.2 \cdot 10^6$	$1.7 \cdot 10^6$	132.8	217.9
	NSD	$4.3 \cdot 10^6$	$6.9 \cdot 10^5$	97.3	162.7
	SD/NSD	1.7	2.5	1.4	1.3

measured. Concerning the May 2014 campaign, days characterized by frequent precipitation events (period 26–30 May) showed an average number concentration of aerosol in the range 0.5–10 μm , slightly higher with respect to days with no precipitation ($6.80 \cdot 10^6 \text{ m}^{-3}$ and $3.81 \cdot 10^6 \text{ m}^{-3}$, respectively). We note that prevalently the rainfall intensity was low ($\approx 0.4 \text{ mm h}^{-1}$). Only in a few cases of precipitation events did we note a remarkable INP decrease in the PM₁₀ fraction at $S_w = 1.01$ (26 May, 8 a.m. and 1 p.m.; 27 May, 1 p.m.). The non regular relationship between INP concentrations and precipitation is due to the complexity of the aerosol scavenging processes and possible additional phenomena, like evaporation of droplets in clouds or near the ground, which can influence INP concentrations (Cotton and Field, 2002; Field et al., 2001; Rosinski and Morgan, 1991).

A fall in INP concentration before and after precipitation has been reported by several authors associated with high rainfall (Bertrand et al., 1973; Bigg and Miles, 1964; Jiang et al., 2015). Hobbs and Locatelli (1970) observed that in many cases rain showers occurred without being accompanied by any significant increases in ice nucleation. Several authors reported an increase in INP concentration at ground level at the onset of rain (Buscaglione, 1968; Hobbs et al., 1968; Ryan and Scott, 1969) probably due to release of ice nuclei by the evaporation of small drops between cloud base and ground or during fog dissipation. Bigg et al. (2015), Huffman et al. (2013) and Prenni et al. (2013) showed that the ground level INP concentrations in a forest ecosystem were enhanced during rain events, and that a fraction of these were biological. A similar result was obtained by Hara et al. (2016) in a forested site in Japan. Biological particles, which become a source of INP, can be released during precipitation and during periods of high humidity through mechanisms such as spore release from fungi, mechanical ejection of bacteria and spores from leaf surfaces, and pollen release and fragmentation during wet weather. Wang et al. (2012) performed irrigation experiments of soil surface and found that intensive water impaction is sufficient to cause ejection of airborne soil organic particles from the soil surface. The importance of soil organic matter as strong ice nuclei has been reported in laboratory and field studies (Schnell and Vali, 1972).

In our case the rainfall intensity was low, and we did not measure an increase of INP during these events. Therefore, we conclude that soil (and associated bio-particles) emission triggered by precipitation was not an important source of INP during the two campaigns.

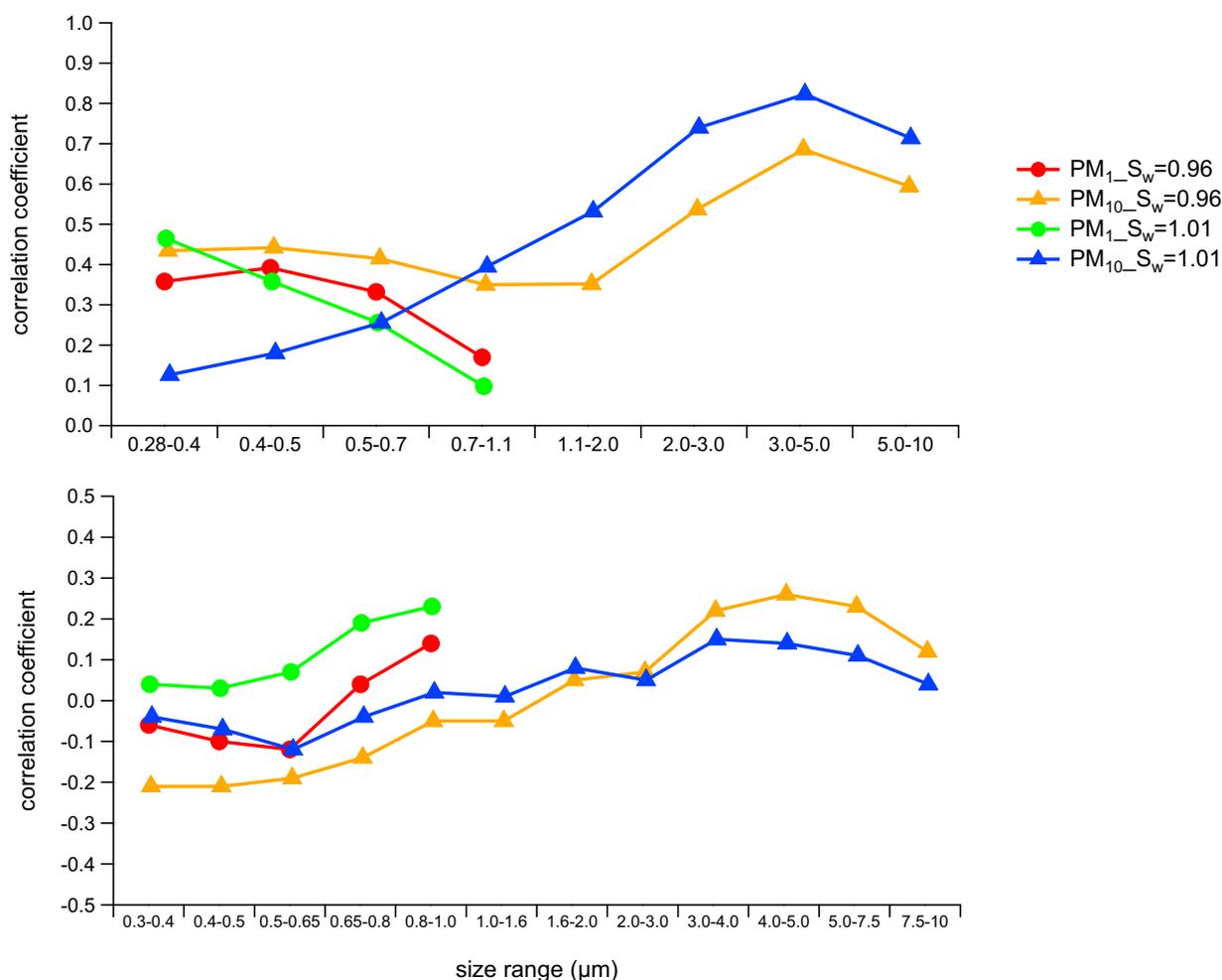


Fig. 7. Correlation coefficient between INP and particle number concentration as a function of the particle size range during the first (top) and second (bottom) campaign.

4. Conclusion

The main conclusions of the campaigns performed at San Pietro Capofiume near Bologna in the periods 10–21 February 2014 and 19–30 May 2014 can be summarized as follows:

- Prevalently higher average INP concentrations were measured in the morning with respect to the afternoon, in the PM_1 fraction with respect to PM_{1-10} and at water super-saturation with respect to water sub-saturation. Only in the first campaign, at $S_w = 1.01$, there was a prevalence of $INP_{PM_{1-10}}$ (coarse fraction) with respect to INP_{PM_1} . This is due to both lower nucleation of fine particles and higher nucleation of coarse particles. The latter is likely related to the presence of carbonaceous particles from biomass burning emissions (which are poor ice nucleus), while the enhanced nucleation efficiency of coarse particles is difficult to explain without a detailed chemical and mineralogical characterization.
- The aerosol in the coarse size range contributed significantly to the total INP concentration. In the first campaign, the INP concentration from the coarse fraction was 28% of the total at $S_w = 0.96$, and 80% at $S_w = 1.01$, in the morning. In the afternoon, the contribution was 38% and 74%, respectively. In the second campaign, the contribution of the coarse size fraction (1–10 μm) to the INP number concentration was lower. These results confirm the conclusion obtained in a previous campaign (09–12 July 2007). On the whole, the results show that the freezing activity of aerosol diameters larger than 1 μm need to be measured to obtain the entire INP population.
- During both campaigns Sahara dust events (SDEs) took place. Results show that the averaged particle number concentration is higher during SDEs than during NSDEs. The average INP concentration in the SDEs and NSDEs were comparable in the PM_1 and in the PM_{10} fractions ($S_w = 1.01$) for the February campaign, while in the second campaign the INP concentration in the PM_{10} fraction was higher in SDEs. The measured and sampled aerosol can include both local sources and mineral dust transported from desert regions. Published measurements performed at high level (such as Chou et al. (2011) at Jungfraujoch) show that SDEs in that site are characterized by a high increase in aerosol and INP number concentration. This depends on the fact that in this case the Saharan dust introduced in the upper layer involves direct transport, or transport possibly diverted by anticyclonic or cyclonic rotation, while sampling at ground level also involves dry and wet deposition processes.
- In our campaigns a low correlation between INP and total aerosol number concentrations was generally observed. On the contrary, significant correlation was observed between coarse particles and INP concentration in the same fraction, with peak correlation in the 3–5 μm size range, during the first campaign. This suggests that particles, with diameter above 2–3 μm , were major contributors to the super-micron INP population. The overall low correlation observed between INP and aerosol number may depend on the variety of parameters related to the ice nucleation processes. In addition, SDE particles transported over long distances can undergo aging processes, thereby influencing the ice nucleation efficiency of mineral dust.
- Precipitation events influence the aerosol concentration. In the February campaign, lower values of INP and particle concentrations were measured in case of rain events. Concerning the May 2014 campaign, days characterized by frequent precipitation events (period 26–30 May) showed an average aerosol number concentration in the range 0.5–10 μm , slightly higher with respect to days with no precipitation. Prevalently the rainfall intensity was low. Only in a few cases of precipitation events did we note a sharp drop in INP in the PM_{10} fraction at $S_w = 1.01$ (26 May, 8 a.m. and 1 p.m.; 27 May, 1 p.m.).

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