Ground level ice nucleating particles measurements at Capo Granitola, a Mediterranean coastal site

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ABSTRACT

This study presents near-surface measurements of ice nucleating particle (INP) concentrations at a ground level Mediterranean site (Capo Granitola, CGR), located in southern Sicily. A coastal area like CGR can be influenced by marine and anthropogenic aerosols, and even by Saharan dust. To obtain the INP concentration in the PM_1 and PM_{10} fractions, an experimental campaign was carried out in April 2016 at the WMO/GAW "I-AMICA" Observatory. Aerosol was sampled on nitrocellulose membranes twice a day. INP concentrations were detected by a dynamic filter processing chamber (DFPC), a replica of the Langer dynamic chamber, at -18°C and -22°C activation temperatures, at different conditions of supersaturation with respect to ice and water.

The sampling period was characterized by three main wind directions, along the coast (from North-West and from South-East), during daytime, and mainly from the land side during the night. INP concentration, in the PM_{10} size fraction, ranged 0.5-27, 3.3-65 and 13-115 m^{-3}, at -18°C below water saturation, at -18°C at water supersaturation and at -22°C at water supersaturation, respectively.

Two weak dust transport events occurred during the experimental campaign, both characterized by an increase in coarse particle number and PM_{10} concentration, not associated with fine particles or other pollutants. Air mass back-trajectories, during the events, were observed to originate from the North African region.

35 Results of the experimental campaign were compared with INP concentrations previously measured
36 at San Pietro Capofiume, a rural site in the Po Valley, and at Mt. Cimone ("O. Vittori" Italian Climate
37 Observatory, 2165 m a.s.l) in the northern Apennines. Both INP concentrations, in the PM_1 and PM_{10}
38 fractions, and activated fractions, at CGR, were prevalently lower than the concentrations obtained at
39 the other two sites. This may be, likely, related to the lower nucleation efficiency of soluble marine
40 aerosols and aged dust particles, partly coated and mixed with hygroscopic material, at CGR.
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43 *Key-words:* Ice nucleating particles; Heterogeneous freezing; Saharan dust transport; Particle number
44 concentration
45

1. Introduction

Ice crystals in the atmosphere have a major impact on precipitation formation and on the microphysical and optical properties of clouds. Ice can nucleate homogeneously from supercooled droplets (pure water or solution) at $T \leq -38°C$, or heterogeneously at much higher temperature, as the phase change is favoured by the presence of solid particles, known as ice nucleating particles (INPs). In general, INPs can be of natural (e.g., mineral dust, volcanic ashes, terrestrial biogenic material, etc.) and anthropogenic (e.g., industrial processes, biomass burning, etc.) origin (Hoose and Möhler, 2012, Murray et al., 2012). Even sea water is a source of ice active organic matter (Knopf et al., 2011, 2018; Wang et al., 2015; Wilson et al., 2015; DeMott et al., 2016; McCluskey et al., 2017; Vergara-Temprado et al., 2017), likely water insoluble in nature and transferable to the atmosphere within sea spray particles (Facchini et al., 2008). In the upper atmosphere ice formation occurs homogeneously or by deposition of water vapour on micron-size aerosol particles (Heymsfield et al., 2017), while condensation/immersion freezing is thought to be the most important ice-formation mechanism for mixed phase cloud (deBoer et al., 2011; Westbrook and Illingworth, 2013).

Although INP represent approximately only 1 in 10^5 ambient particles in the troposphere, with greater concentrations at colder temperature and higher supersaturation (Rogers et al. 1998), they can rapidly transform a liquid-dominated cloud into an ice-dominated cloud via the Wegener–Bergeron–Findeisen process (Korolev, 2007), thereby modifying the cloud's precipitation rates, lifetime, and radiative properties. The ice phase favours precipitation as it can grow much more quickly than liquid droplets (McFarguhar et al., 2017). Most precipitation at middle and high latitude comes from cold clouds containing ice particles (Heymsfield, 2006).

Few publications report INP observations from the Mediterranean basin (Prodi et al., 1983, Levi and Rosenfeld, 1996; Ardon-Dryer and Levin, 2014; Schrod et al., 2017). Santachiara et al. (2010) and Belosi et al. (2017) carried out INP measurements in different size classes of aerosol (PM_1 and PM_{10}) at a rural site, San Pietro Capofiume (SPC) in the Po Valley basin, near Bologna. Their papers suggest, among other things, that supermicron aerosol particles are a significant component of the INP population, in agreement with several past and recent studies (e.g., Mason et al. 2016; Si et al., 2018). Rinaldi et al. (2017) performed INP measurements during May 2014 and October 2015 at the top of Mt. Cimone (CMN, 2165 m a.s.l.), the highest peak of the north Italian Apennines that can be considered representative of the Mediterranean basin free tropospheric background, with a superimposed direct influence of the polluted Po Valley in specific periods. Their analysis of meteorological parameters, gaseous tracer concentrations and backward trajectories suggest that

79 transport processes occurring at different spatial scales, from local to synoptic, contribute to the INP
80 population at the high altitude station.

81 The objective of the present study was to measure INP concentrations at a ground level Mediterranean
82 site (Capo Granitola, CGR), a GAW Regional Station located in southern Sicily, to extend the limited
83 number of INP observations over the central Mediterranean Sea. A coastal area like CGR can be
84 directly influenced by marine aerosol, as well as anthropogenic emissions, and even by Saharan dust.
85 Aerosol particles can be modified chemically and physically after being released into the atmosphere
86 through a variety of processes occurring in the troposphere. In general, laboratory experiments of
87 particle treatment (e.g. coating) led to a decrease in INP ability compared to uncoated particles,
88 namely in the deposition mode (Hoose and Möhler, 2012; Kanji et al, 2013). This suggests that
89 chemical aging in the atmosphere will also lead to a decreased INP concentration due to
90 heterogeneous freezing processes (Ansmann et al., 2008; Niedermeier et al., 2010; Kanji et al., 2017).
91 Given the multiple sources characterizing the site, CGR can be an ideal location to observe the effect
92 of aging and mixing on the ice nucleation activity of aerosol particles in the real atmosphere.

93 The INP concentrations obtained at CGR were related to aerosol sources and meteorological
94 conditions and compared with available measurements in the Mediterranean basin, a recognized
95 hotspot region both in terms of climate change and air quality.

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97 **2. Material and methods**

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99 The experimental campaign was carried out in the period 08-25 April 2016 at the I-AMICA Capo
100 Granitola Climate Observatory (37.66670° N, 12.65000° E; 5 m a.s.l.), located 12 Km to the South-
101 East from Mazara del Vallo (Cristofanelli et al., 2017). CGR is a remote site, directly exposed to the
102 Strait of Sicily, which makes the site ideal for monitoring the marine background conditions and the
103 Saharan dust transport from North Africa towards Europe. Moreover, being overlooking the
104 Mediterranean sea, it is a perfect site for studying marine aerosols, fresh and transported over long
105 distances. The Observatory was installed in 2014 and is continuously run by the Institute for
106 Atmosphere Sciences and Climate of the Italian National Research Council (ISAC - CNR). The
107 observatory carries out continuous atmospheric composition measurements representative of western
108 Sicily/central Mediterranean basin. It frequently encounters air masses that are representative of
109 background conditions in the Mediterranean basin and provides useful hints to investigate the
110 influence of specific atmospheric processes (e.g. long-range transport, mineral dust emission from
111 Northern Africa, ship emissions). Details of the continuous measurements and instrumental set-up
112 are given in Cristofanelli et al. (2017). The routine set of measurements carried out at the CGR

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observatory was implemented with a specific measurement program during the AIR-SEA Lab campaign object of this paper. This included aerosol size distribution from 0.2 μm to 20 μm obtained from an optical particle spectrometer (OPC, FAI Multichannel Optical Particle Counter Monitor) and sampling for aerosol chemical characterization. Aerosol samples were collected by a Berner cascade impactor (flow rate 80 L min^{-1}), segregating particles in the following intervals: (1) 0.06-0.14, (2) 0.14-0.42, (3) 0.42-1.2, (4) 1.2-3.5 and (5) 3.5-10 μm of aerodynamic diameter. The particles were collected on aluminum and Tedlar foils as described in Sandrini et al. (2016) and Matta et al. (2003). A 24 h time resolution was adopted with sampling starting at 9:00 a.m. (UTC+1 time).

The Tedlar substrates were extracted in 10 mL of Milli-Q water for 30 min in an ultrasonic bath. The extracts were analyzed by ion chromatography to quantify water soluble inorganic species (Cl$^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+} and Ca^{2+}) and organic acids (acetate, formate, methanesulfonate and oxalate). A TOC 5000-A analyzer (Shimadzu, Japan) was used to determine water soluble organic carbon (WSOC). Details on the analytical procedures can be found in Sandrini et al. (2016). The aggregated concentrations discussed in this work were obtained by summing up the concentrations measured in the first three stages (0.06-1.2 μm: ~PM$_1$) and in all the stages (0.06-10 μm: PM$_{10}$) of the impactor. The aerosol water soluble fraction was obtained by summing up the concentration of all the inorganic ionic species and WSOC. A mass-to-carbon conversion factor of 1.8 was applied to WSOC concentration to account for the mass of water soluble organics. By using this approach, we reasonably accounted for all water soluble aerosol mass. The water insoluble fraction, mainly representing the contribution of mineral or soil dust in the sampled aerosol, was estimated by subtracting the mass of the analyzed soluble species, from the PM$_1$ and PM$_{10}$ mass concentrations derived from the OPC.

To obtain the INP concentration the PM$_1$ and PM$_{10}$ aerosol fractions were sampled on nitrocellulose membrane (Millipore HABG04700, nominal porosity 0.45 μm) twice a day (00:00 a.m. - 12:00 a.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 60 min. Aerosol fractions were sampled by inserting different sampling heads (1 μm, and 10 μm cut-point-Standard EN 12341, TCR Tecora) in front of the filter. Meteorological data (air temperature, relative humidity, wind speed and direction, atmospheric pressure) were recorded by an integrated weather station Vaisala WXT 520.

INP concentrations were quantified in the lab, after completion of the campaign, by the membrane filter technique (Bigg, 1963, 1990; Lala and Jiusto, 1972; Vali, 1975) following the procedure shown in Santachiara et al. (2010). Here we summarize the main points. Filters were placed on 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, different water saturation ratios (S_w) could be obtained. Measurements were performed at -18°C and -22°C, and at 1.02 water saturation ratio. At -18°C INP concentrations were obtained even at S_w = 0.96. Uncertainties for temperature and S_w are about 0.1°C and 0.02, respectively. The estimated INP measurement uncertainty of the DFPC is ±30% (DeMott et al., 2018). Examples of inter-comparisons between the DFPC and other INP quantification techniques can be found in deMott et al. (2018) and McCluskey et al. (2018).

3. Results

3.1. Campaign general features and particle number concentration

Local emissions influence CGR on average during 4% of the time, nearby sources in 39% and remote sources in 31%, while background conditions were observed in 26% of cases, as highlighted trough multi-year O_3/NO_x variability by Cristofanelli et al. (2017). Most of the background O_3/NO_x were observed during daytime when offshore air masses usually affect the measurement site.

Under the meteorological point of view, April 2016 was characterized by typical spring conditions with average temperature, pressure, relative humidity (RH) and wind speed equal to 4.9±3.0 °C, 1012±12 hPa, 70±14 % and 4.9±3.0 m s^{-1}, respectively. Three main wind directions were identified during the observation period, along the coast (from North-West and from South-East) during daytime, and mainly from the land side (and South-East) during the night.

The campaign was characterized by more instable conditions at the beginning and at the end (8-12 and 20-25 April), with higher wind speed and lower temperature, and by a period (13-20 April) in the central part, characterized by higher atmospheric pressure. The latter was characterized by progressive accumulation of pollutants (Fig. 1) and by the occurrence of two dust transport (DT) events. Said (weak) events were identified on 13th and 17/18th April by an increase in PM$_{10}$ concentration and coarse particle number, not associated with an increase of fine particles (D_p < 1 μm) or other pollutants (see further on for details).

Particle number concentrations show no appreciable diurnal trend for fine particles, while coarse particles present higher concentrations at night (about 20% increase, in average). This is consistent with the multi-year characterization by Cristofanelli et al. (2017), showing higher contribution from inland sources at night.

181 Figure 2 shows the daily PM_{10} insoluble and soluble aerosol fractions during the experimental

182 measurement period. The insoluble fraction was obtained by subtracting the measured soluble

183 fraction from the PM_{10} aerosol concentration obtained from the OPC data. Increases in the insoluble

184 PM_{10} aerosol fraction are clearly visible during the DT events.

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186 *3.2 INP concentration*

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188 Table 1a gives the average INP concentrations, in the PM_1 and PM_{10} fractions, and the average

189 contribution of the coarse aerosol fraction, obtained during the campaign at the different conditions

190 (standard deviation, SD, is reported in brackets).

191 The increase in INP from PM_1 to PM_{10} was small at $T = -18°C$, $S_w = 0.96$, and grew at $T = -18°C$, S_w

192 $= 1.02$, and at $T = -22°C$, $S_w = 1.02$. The difference between the INP concentrations in the PM_1 and

193 PM_{10} size intervals is statistically significant for the latter two conditions ($p<0.01$). Considering all

194 the samples, the average contribution of the coarse fraction to total INP increased significantly

195 ($p<0.05$) from 23% at $-18°C$ and $S_w= 0.96$ to 49% at $-22°C$ and $S_w = 1.02$. Table 1b shows the average

196 INP concentrations and SD, separately for night and day sampling periods.

197 Fig. 3 shows the daily average INP concentrations in the PM_{10} aerosol size fraction at the different

198 activation temperatures and saturation conditions probed during the experiment.

199 The INP daily average concentration in the PM_{10} fraction ($T= -22°C$; $S_w=1.02$) was in the range 19-

200 83 m^{-3}. The highest INP concentration at $-22°C$ was measured on 13th April (12:00 a.m.) during one

201 of the above-mentioned DT events. Due to the position of CGR, events showing a separate marine or

202 terrestrial aerosol source are infrequent and samples collected at the station prevalently consist of

203 mixed aerosol sources, as air masses cross both sea and land prior to reaching the sampling site. It

204 can be observed that the INP concentrations in the PM_{10} fraction at $S_w = 1.02$ are generally

205 comparable between $T= -18°C$ and $T = -22°C$, particularly at the end of the campaign, while a higher

206 discrepancy between the concentration at $T = -22°C$ and at $T = -18°C$ was observed during the DT

207 events. This suggests a higher sensitivity to temperature of mineral dust with respect to marine and

208 local aerosol particles. A high increase of INP concentration was measured at $T = -18°C$ from

209 subsaturated (deposition freezing) to supersaturated conditions (condensation freezing) with respect

210 to water.

211 Figure 4 shows the concentration of INPs in the coarse fraction, obtained by subtracting the PM_1

212 value from the PM_{10} one. Missing bars in Figure 4 indicate virtually no contribution from coarse INP,

213 i.e., the concentrations in the PM_1 and PM_{10} size fractions are comparable, within the measurement

214 uncertainty. The concentration of coarse INPs on 9th April and for the final part of the campaign are

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215   prevalently comparable, or higher, at T = -18°C compared with T = -22°C. Figure 2 shows that the

216   contribution of the water-soluble aerosol fraction tends to increase toward the end of the campaign,

217   with contributions higher than 50% on the last three days (23th, 24th and 25th April). Unfortunately,

218   no chemical composition information are available for 9th April. The above suggests that the

219   activation temperature dependency of the INP concentrations, in the coarse mode, tends to decrease

220   when aerosol particles are characterized by a higher fraction of soluble components. A more

221   quantitative analysis shows a moderate (but not significant) positive correlation between the

222   contribution of the water-insoluble aerosol fraction and the difference in the INP concentration

223   between -22 and -18°C (R = 0.28), which seems to support the above statement. The dataset of

224   observations at CGR is clearly too limited to allow firm conclusions on this regard, nevertheless, a

225   similar behaviour for ice nucleation in presence of water-soluble aerosol components has been

226   documented in previous studies (Hoose and Moehler, 2012; Kanji et al, 2013; Knopf et al., 2018;

227   Paramanov et al., 2018).

228   Table 2 shows the activated fraction (AF) of PM_1, PM_{10} and of the coarse aerosol fraction separately

229   for night and day sampling periods. The higher AF values were associated with coarse particles (as

230   expected; significant difference, $p<0.05$) and, to a lesser extent, in night-time samples, when aerosol

231   particles were mainly coming from inland, even though the only statistically significant difference

232   between day and night samples was observed at T=-18°C, in super-saturated conditions ($p<0.05$).

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234   *3.3 Dust Transport events*

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236   During the campaign, two weak Sahara DTs events took place, one on 13th April and the second

237   between 17 and 18 April. During these events, average PM10 mass concentrations as high as 33±16

238   µg m^{-3} and 34±12 µg m^{-3} were observed, respectively, against an average of 13±7 µg m^{-3} for the rest

239   of the campaign. Coarse particle number concentration increased 2.3 times during the DT events,

240   while submicron particle number showed an increase of only 1.4 times. Figure 5 shows the backward

241   trajectories on 13th and 18th April, both at 12:00 a.m. (UTC time), calculated by the NOAA HYSPLIT

242   model (Rolph et al., 2017).

243   Air mass back-trajectories showed an origin (or passages) in the North African region. The

244   identification of the two DT events was also confirmed by the satellite observations from

245   MODIS/terra, showing an increase in Atmospheric Optical Depth in the Mediterranean region, from

246   the Libyan coast grazing the coastlines of Sicily and Southern Italy (not shown).

247   By considering the first event, INP measurements in the PM_{10} fraction carried out at T = -22°C and

248   S_w = 1.02 better evidence and confirm the transport of Sahara dust. We observed an increase in INP,

249   prevalently due to the coarse fraction, starting on 13th April at 00:00 a.m. (50 m^{-3}), a further high

250   increase on 13th April at 12:00 a.m. (115 m^{-3}), and a subsequent gradual decrease on 14th April at

251   00:00 a.m. (51 m^{-3}), and at 12:00 a.m. (15 m^{-3}). This trend was less evident at T = -18°C at S_w = 1.02,

252   and absent at T = -18°C , S_w = 0.96. The PM$_{10}$ activated fraction followed the same trend as the INP

253   concentration.

254   The second DT event took place from 12:00 a.m. on 17th April until 10:00 a.m. of the following day.

255   During this event, only INP measurement on 18th April (12:00 a.m.) were available. Although the

256   particle number concentration shows a significant increase in this period, both in the fine and coarse

257   fractions, the corresponding INP concentrations and AF do not follow the trend, in both PM$_1$ and

258   PM$_{10}$ size ranges. The only common feature between the two DT events is the high difference between

259   coarse INP concentration at T=-22°C with respect to T=-18°C (Fig. 4), which seems to be related

260   with the ice nucleating properties of mineral dust particles.

261

262   *3.4 INP in the Mediterranean basin*

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264   Measurements of INP concentration in the Mediterranean basin are scarce. Table 3 shows the INP

265   concentrations obtained in previous campaigns at SPC (Belosi et al., 2017), at CMN (Rinaldi et al.,

266   2017) and CGR (present study). Results are given in supersaturation conditions with respect to water

267   (S_w = 1.02) at the given temperatures. The SD of the concentrations are shown in brackets. The INP

268   concentrations in the PM$_1$ and PM$_{10}$ fractions at CGR were prevalently lower than the values obtained

269   by Rinaldi et al. (2017), and Belosi et al. (2017) at the mountain and rural sites in the Po Valley (CMN

270   and SPC, respectively). In addition, the AF observed at CGR (Table 2) is at least one order of

271   magnitude lower than the values reported for the continental locations (Belosi et al., 2017; Rinaldi et

272   al., 2017). The lower INP concentrations and tendency of aerosol particles to nucleate ice observed

273   at the coastal site of CGR, with respect to continental locations, may be due to the higher influence

274   of soluble components from marine aerosols, as discussed previously.

275   In addition, Table 3 also shows INP concentration ranges obtained at other sites in the Mediterranean

276   basin (Tel Aviv, Cyprus and the Eastern Mediterranean Sea). These concentration values give an idea

277   of the different INP concentrations that can be met in the Mediterranean basin. It is worth highlighting

278   that for a proper quantitative comparison with the results of the present study, information on the total

279   particle concentration during the measurements would be also necessary, which are not always

280   available.

281   Prodi et al. (1983) measured the INP concentration at -18°C with a static diffusion chamber in

282   conditions of water supersaturation (condensation mode) during a cruise along the eastern part of the

283   Mediterranean Sea, Red Sea and Indian Ocean. INP concentrations between $3x10^2$ m^{-3} and 10^3 m^{-3}

284   were measured in the Mediterranean Sea. Levi and Rosenfeld measured INP concentrations at Har-

285   Gilo (7 km South of Jerusalem) and at Ashdod, a coastal site near Tel Aviv, during rainy periods.

286   They found concentrations between 100 and 270 m^{-3} depending on the movements of the rain cloud

287   systems. Ardon-Dryer and Levin (2014) measured the INP concentration in immersion freezing mode

288   in the eastern Mediterranean region at Tel Aviv (University campus). The INP concentrations in case

289   of "clean" days and dust storms at -18°C were in the range $0.4x10^3 - 10^4$ m^{-3} and $3x10^3 - 3x10^4$ m^{-3},

290   respectively; at lower temperature (-22°C) the INP concentrations on days with dust storms ranged

291   from $20x10^3$ to $200x10^3$ m^{-3}, while on clean days conditions ranged from 10^3 to $80x10^3$ m^{-3}. Also the

292   recent work by Zipori et al. (2018) shows the importance of mineral dust in ice cloud formation in

293   northern Israel.

294   Schrod et al. (2017) measured the abundance of INPs in the lower troposphere from unmanned

295   aircraft systems during an intensive field campaign on aerosol, clouds, and ice nucleation in the

296   Eastern Mediterranean (Cyprus) in April 2016. They found an INP concentration of about 10^3 m^{-3} (T

297   = -30°C) with an AF between $5x10^{-5}$ at -20°C and 10^{-4} at -25°C at S_w = 1.01. It is worth highlighting

298   that these measurements were almost simultaneous to those presented here. The high AF observed at

299   Cyprus at comparable temperatures suggest significant differences in the aerosol sources at the two

300   sites, with mineral dust being likely much more important at Cyprus, as clearly pointed out by Schrod

301   et al. (2017).

302   All reported measurement sites (Tel Aviv, Cyprus and Eastern Mediterranean Sea) are influenced by

303   a large contribution of mineral dust. Therefore, these INP concentrations should be considered

304   specific to the Eastern part of the Mediterranean basin characterized by frequent transport of mineral

305   dust particles. By contrast, excluding the specific weak Saharan DT events, during the campaign,

306   GCR was prevalently influenced by marine emissions and aged anthropogenic aerosols.

307   Figure 6 shows the INP concentration, in the PM_{10} aerosol fraction as a function of the activation

308   temperature for CMN (2nd campaign, Table 3), CGR and SPC (for this location INP concentrations

309   were available at only one temperature value).

310   The slopes of the interpolation lines for CMN and CGR, between -18°C and -22°C, are consistent

311   with each other and also with the results of DeMott et al., (2010), as already reported by Rinaldi et

312   al. (2017). Considering this slope, and assuming it is applicable also to SPC data, it is possible to

313   extrapolate INP concentrations at -15°C for the three sites (open symbols in Fig. 4). This temperature

314   value was considered by Vergara-Temprado et al. (2017) in their global modelling work, for

315   predicting INP concentration in mixed-phase clouds, based on laboratory and field measurements of

316   ice nucleation by K-feldspar (an ice-active component of desert dust) and marine organic aerosols

317 (from sea spray). From Fig. 6, it can be seen that, at -15°C, average INP concentration value of 16 m$^-$
318 ^{3}, 29 m^{-3} and 165 m^{-3} can be extrapolated for CGR, CMN and SPC, respectively. These values are
319 consistent with the annual mean INP concentration value predicted by Vergara-Temprado et al.
320 (2017) for the Mediterranean basin, which is between 50 m^{-3} and 100 m^{-3}.

321

4. Conclusions

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324 Near-surface INP concentrations in the PM$_1$ and PM$_{10}$ size fractions were measured at a coastal
325 Mediterranean site (Capo Granitola), located in southern Sicily, during April 2016. Ice activation was
326 performed in sub- and super-saturated conditions with respect to water and at different temperatures.
327 Due to the position of CGR and to the sampling duration, events showing a separate marine or
328 terrestrial aerosol source were infrequent and samples consisted mainly of mixed aerosol sources, as
329 air masses crossed both sea and land before reaching the sampling site.
330 Observed INP atmospheric concentrations range between 0.5 and 115 m^{-3}, increasing with decreasing
331 activation temperature and from sub-saturated to super-saturated conditions with respect to water.
332 The results confirm the large contribution of the coarse particles to the INP population, with
333 increasing contribution (from 23% to 57%) by decreasing activation temperature and increasing
334 supersaturation.
335 Two weak Saharan DT events were observed during the campaign. During the events modest increase
336 of coarse particle numbers and INP concentrations were observed. An interesting common feature of
337 the two DT events is the high difference between INP concentration in the PM$_{10}$ fraction at T = -22°C
338 with respect to T = -18°C, which suggests a high sensitivity to temperature of mineral dust.
339 The INP concentration in the PM$_1$ and PM$_{10}$ fractions at CGR was significantly lower than those
340 obtained by Rinaldi et al. (2017), and Belosi et al., (2017) at two other Mediterranean sites,
341 characterized by more continental character, CMN and SPC, respectively. In addition, the AF
342 observed at CGR was at least one order of magnitude lower than the values reported for the above
343 continental locations. The lower tendency of aerosol particles to nucleate ice at the coastal location
344 may likely be due to the higher influence of soluble components from marine aerosols, as pointed out
345 in the literature.
346 By extrapolating the INP concentrations obtained at CGR, CMN and SPC at -15°C, we obtained INP
347 concentrations comparable with the annual mean average estimate given by Vergara-Temprado et al.
348 (2017) for the Mediterranean basin. However, as some experimental findings suggest, other parts of
349 the Mediterranean basin are influenced by frequent transport of large quantities of mineral dust and
350 are characterized by much higher INP concentration levels.

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Acknowledgments

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364 **Tables**

365

366 Table 1a. Average INP concentrations and standard deviation (SD) obtained during the campaign. In

367 brackets are reported the SD values. The number of samples (n) is 29. INP_{coarse} contribution indicates

368 the fractional contribution of INP in the coarse particle size range over the total, calculated as (INP_{PM10}-

369 INP_{PM1})/INP_{PM10}

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	INP_{PM1} (m^{-3})	INP_{PM10} (m^{-3})	INP_{coarse} contribution
-18°C; S_w = 0.96	4.6 (3.5)	6.0 (6.1)	0.23±0.33
-18°C; S_w =1.02	13.0 (9.2)	24.1 (16.3)	0.40±0.32
-22°C; S_w = 1.02	17.8 (10.6)	41.2 (20.5)	0.49±0.37

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373

374 Table 1b. Average INP concentrations and SD for night and day conditions. In brackets are reported

375 the SD values. For night samples, n = 15, for Day samples, n = 14.

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	INP_{PM1} (m^{-3})	INP_{PM10} (m^{-3})	INP_{coarse} contribution
Night			
-18°C; S_w = 0.96	4.0 (1.8)	6.3 (7.2)	0.22±0.34
-18°C; S_w = 1.02	11.4 (9.4)	27.8 (18.9)	0.49±0.33
-22°C; S_w = 1.02	19.0 (12.8)	41.4 (15.1)	0.50±0.38
Day			
-18°C; S_w = 0.96	5.3 (4.6)	5.7 (4.9)	0.24±0.32
-18°C; S_w =1.02	14.7 (9.0)	20.1 (12.5)	0.29±0.29
-22°C; S_w = 1.02	16.4 (7.6)	41.0 (25.6)	0.46±0.40

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Table 2. AF of PM$_1$, PM$_{10}$ and coarse aerosol fractions; the whole campaign, night and day sampling periods. Campaign, n = 29; Night, n= 15; Day, n = 14.

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	AF$_{PM1}$	AF$_{PM10}$	AF$_{Coarse}$
Campaign			
-18°C S$_w$: 0.96	2.3×10^{-7} (1.9×10^{-7})	3.1×10^{-7} (3.9×10^{-7})	3.0×10^{-6} (3.8×10^{-6})
-18°C S$_w$: 1.02	7.1×10^{-7} (6.1×10^{-7})	1.2×10^{-6} (1.0×10^{-6})	8.3×10^{-6} (8.7×10^{-6})
-22°C S$_w$: 1.02	8.9×10^{-7} (7.0×10^{-7})	1.9×10^{-6} (1.1×10^{-6})	1.2×10^{-5} (0.94×10^{-5})
Night			
-18°C S$_w$: 0.96	2.1×10^{-7} (1.0×10^{-7})	3.3×10^{-7} (4.4×10^{-7})	3.4×10^{-6} (4.6×10^{-6})
-18°C S$_w$: 1.02	5.9×10^{-7} (4.4×10^{-7})	1.4×10^{-6} (1.2×10^{-6})	1.0×10^{-5} (1.1×10^{-5})
-22°C S$_w$: 1.02	1.0×10^{-6} (0.72×10^{-6})	2.0×10^{-6} (1.1×10^{-6})	1.3×10^{-5} (1.0×10^{-5})
Day			
-18°C S$_w$: 0.96	2.6×10^{-7} (2.6×10^{-7})	2.8×10^{-7} (3.6×10^{-7})	2.5×10^{-6} (3.0×10^{-6})
-18°C S$_w$: 1.02	8.3×10^{-7} (7.5×10^{-7})	9.5×10^{-7} (8.0×10^{-7})	5.8×10^{-6} (3.9×10^{-6})
-22°C S$_w$: 1.02	7.5×10^{-7} (6.7×10^{-7})	1.8×10^{-6} (1.2×10^{-6})	1.1×10^{-5} (0.85×10^{-5})

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399 Table 3 – INP concentrations and SD (in brackets) of measurements carried out at Mediterranean
400 sites.
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Source	INP$_{PM1}$	INP$_{PM10}$
	m^{-3}	m^{-3}
CMN 1st camp.(DFPC) -18°C, Rinaldi et al., 2017	64 (4)	86 (49)
CMN 2nd camp.(DFPC) -18°C, Rinaldi et al.,2017	12 (19)	43 (32)
CMN 2nd camp. (DFPC) - 22°C, Rinaldi et al., 2017	-	71 (76)
SPC 1st camp. (DFPC) -18°C, Belosi et al.,2017	69 (35)	310 (213)
SPC 2nd camp. (DFPC) - 18°C, Belosi et al., 2017	107 (51)	171 (82)
SPC (DFPC) -17°C, Santachiara et al., 2010		110 (112)
CGR (DFPC) - 18°C - Present study	13 (9.2)	24 (16.3)
CGR (DFPC) - 22°C - Present study	18 (10.6)	41 (20.5)
Eastern Mediterranean sea (Static diffusion chamber) - 18°C, Prodi et al., 1983	-	300 - 10^3
Har-Gilo and Ashdod - Israel (Static diffusion chamber) - 15°C, Levi and Rosenfeld (1996)	-	100 - 270
Tel Aviv (FRIDGE - Immersion freezing) -18°C, Ardon-Dryer and Levin (2014)	-	400 - 3x10^4 [*]
Tel Aviv (FRIDGE - Immersion freezing) -22°C, Ardon-Dryer and Levin (2014)	-	10^3 - 1x10^5[*]
Cyprus (FRIDGE, unmanned aircraft system) - 30°C, Schrod et al., (2017)	-	10^3[*]

402 [*] no size selection aerosol particles; measurements in "clean" conditions (i.e. no dust storms).
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Figure captions

Fig. 1. Particle number concentration (cm^{-3}) in the fine (particle diameter, $D_p < 1$ µm), coarse ($1 < D_p < 10$ µm) and total ($D_p < 10$ µm) size fractions. The data time resolution is 5 minutes. The dotted lines enclose the Saharan dust transport events.

Fig. 2. Daily PM$_{10}$ insoluble and soluble aerosol fractions. The dotted lines enclose the samples influenced by the Saharan dust transport events. Error bars indicate the estimated uncertainty in the determination of the water-soluble and insoluble fractions.

Fig. 3. Daily average INP concentrations in the PM$_{10}$ aerosol size fraction at different temperatures and S_w. The dotted lines enclose the Saharan dust transport events.

Fig. 4. Daily average INP concentrations in the coarse aerosol size fraction at different temperatures. The dotted lines enclose the Saharan dust transport events. Error bars indicate the estimated uncertainty in the determination of the coarse INP concentration.

Fig. 5. The 72-h backward trajectories of air masses arriving at CGR on 13th April 2016 (left) and 18th April 2016 (right).

Fig. 6. INP$_{PM10}$ concentration pattern as a function of the activation temperature at CGR, CMN (Rinaldi et al., 2017) and SPC (Belosi et al., 2016). Empty symbols represent estimated concentrations at -15°C, based on the temperature dependency between -18 and -22°C.

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