Ground based Measurements of Immersion-Freezing in the Eastern Mediterranean

K. Ardon-Dryer[1,2,*] and Z. Levin[1,3]

[1]{Department of Geophysical, Atmospheric and Planetary Sciences, Tel Aviv University, Israel}

[2]{The Porter School of Environmental Studies, Tel Aviv University, Israel}

[3]{Energy, Environment and Water Research Center, The Cyprus Institute, Nicosia, Cyprus}

[*]{Now at: Department of Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, M.A, USA}

Correspondence to: K. Ardon-Dryer (karinard@mit.edu)

Abstract

Ice nuclei were measured in immersion freezing mode in the Eastern Mediterranean region using the FRIDGE-TAU (FRankfurt Ice-nuclei Deposition freezinG Experiment, the Tel Aviv University version) chamber. Aerosols were sampled during dust storms and on clean and polluted days (e.g. Lag BaOmer). The aerosols immersion freezing potential was analyzed in the laboratory using a drop freezing method. Droplets from all the samples were found to freeze between -11.8ºC and -28.9ºC. Immersion-freezing nuclei (FN) concentrations range between $0.16L^{-1}$ to $234L^{-1}$ while the activated fraction (AF) ranges between $8.7x10^{-8}$ to $4.9x10^{-4}$. The median temperature at which the drops from each filter froze were found to be correlated with the corresponding daily average of PM_{10}, $PM_{2.5}$ and PM_{10}-$PM_{2.5}$. Higher correlation value between FN concentrations and PM_{10}-$PM_{2.5}$ suggests that the larger particles are generally more effective as FN.

The measurements were divided into dust storms and clean conditions based on the air mass back trajectories and the aerosol mass concentrations (PM_{10}). Droplets containing ambient particles from dust storm days froze at warmer temperatures than droplets containing particles from clean days. Statistically significant differences were found between dust storms and clean

conditions primarily in terms of the initial temperature at which the first drops froze the median freezing temperature and the aerosol loading (PM values). FN concentrations and AF values in dust storms were larger by more than a factor of two than in the clean conditions. This observation agrees with previous studies showing that some dust particles are almost always present in the atmosphere in this region.

Measurements of aerosol emitted from wood burning bonfires during a Lag BaOmer holiday showed that although high concentration of particles were emitted, their effectiveness as freezing nuclei was relatively poor. The most likely reason for the low FN efficiency is the combination of relatively low fire temperatures and high organic carbon fraction in the aerosols.

1 Introduction

Ice plays an important role in the development of clouds and precipitation and in affecting the planet's albedo (IPCC, 2007). Ice in the atmosphere forms mainly by heterogeneous nucleation on aerosol particles called ice nuclei (IN). Heterogeneous ice nucleation can proceed through a number of mechanisms such as: contact freezing that occurs when an ice nucleus initiates freezing by contacting a supercooled droplet; by condensation freezing that takes place following water condensation on the ice nucleus; by deposition freezing that occurs when an ice embryo forms directly by water vapor condensation on the surface of the particle; by immersion freezing when the IN particle is immersed in the supercooled drop (Pruppacher and Klett, 1997). The concentrations and physical properties of these IN particles vary greatly from place to place and with weather conditions.

The relative importance of the different freezing modes and our understanding of the physical and chemical processes underlying heterogeneous ice formation is limited (Niedermeier et al., 2010). Difficulties arise in quantifying the mechanisms of ice nucleation because of the varied composition, surface characteristics and size distributions of the IN (Kanji et al., 2011). In the last decade much attention has been given to laboratory studies on heterogeneous ice nucleation (e.g. Hoose and Möhler, 2012 and references therein) and to field studies (e.g. DeMott et al., 2003a,b; Prenni et al., 2009a,b; Klein et al., 2010a; Santachiara et al., 2010; Ardon-Dryer et al., 2011; Conen et al., 2012) all of which contributed greatly to our understanding of IN distribution in different parts of the world. In addition, analysis of the chemical composition of IN residuals

from airborne measurements using electron microscopy and mass spectroscopy (e.g. Seifert et al., 2003; Cziczo et al., 2003, 2006, 2013; Froyd et al., 2010) have added a deeper understanding about the nature of some of the IN in the atmosphere.

Although biological particles have been found to be among the most efficient IN (e.g. Schnell and Vali, 1976; Levin and Yankofsky, 1983; Levin et al., 1987; Diehl et al., 2002), their concentrations in the atmosphere are relatively low. This makes them less likely to dominate the ice processes in clouds (Hoose et al., 2010). On the other hand, mineral dust aerosols are among the largest contributors to atmospheric aerosols (Goudie and Middleton, 2006). The presence of dust particles inside many ice crystals suggests that ice nucleation is often initiated by mineral dust aerosols in the atmosphere (Isono, 1955; Isono et al., 1971; Kumai, 1961, 1976; Twohy and Poellot, 2005; Cziczo et al., 2013). In addition, many field studies show an increase of IN concentration during dust storms (e.g. Bowdle et al., 1985; DeMott et al., 2003a; Van den Heever et al., 2006; Chou et al., 2011), with increases as high as double (e.g. Levi and Rosenfeld, 1996) or even fivefold (e.g. Klein et al., 2010a) compared to dust free conditions.

Dust particles have been observed to nucleate ice at different heterogeneous nucleation modes: deposition freezing (e.g. Möhler et al., 2006; Kulkarni and Dobbie, 2010; Kanji et al., 2013), condensation freezing (e.g. Roberts and Hallett, 1968; Levi and Rosenfeld, 1996; Zimmermann et al., 2008; DeMott et al., 2011), contact freezing (e.g. Pitter and Pruppacher, 1973; Ladino et al., 2011) and immersion freezing modes (e.g. Pitter and Pruppacher, 1973; Marcolli et al., 2007; Lüönd et al., 2010; Broadley et al., 2012; Pinti et al., 2012; Welti et al., 2012; Kanji et al., 2013). Zang et al. (2012) concluded that dust particles play an important role in modifying mixed phase cloud properties due to their ability to create ice. Moreover Lohmann and Diehl (2006) using their parameterization of heterogeneous ice nucleation, found that dust particles can have a significant impact on the liquid water path, cloud lifetime, precipitation rate and top of the atmosphere radiation.

Results from extensive IN measurements around the world have been published in the past few decades. However, only very few were reported from the Eastern Mediterranean (e.g. Gagin, 1975; Levi and Rosenfeld, 1996). Gagin (1975) measured the concentrations of condensation freezing nuclei near the bases of cumulus clouds, by using a thermal diffusion chamber at water saturation over the temperature range of -5°C to -25°C. Ground measurements of IN

concentration by Levi and Rosenfeld (1996) using a thermal diffusion chamber at -15°C reported similar IN concentrations to those reported by Gagin (1975). Levi and Rosenfeld (1996) found that the concentration of IN during dust storm periods was more than double than those found during non-dust storm periods. Although immersion freezing has been shown to be the dominant mode of ice nucleation (e.g. Hoose et al., 2010), measurements of IN in this mode from the Eastern Mediterranean area have never been reported.

The aim of the present research is to characterize the efficiency of IN in the Eastern Mediterranean area in immersion freezing mode in dust storm days and during days without dust storms.

2 Characteristics of the research area

The measurements were conducted from Jan 2009 to Dec 2010 in the Eastern Mediterranean region on the Tel Aviv University campus, located in the north part of Tel Aviv, Israel (Fig. 1). The sampling was conducted on the roof top of the Department of Geophysical, Atmospheric and Planetary Sciences (32°6'46.7"N 34°48'22.9"E), about 20m above ground, 60m above sea level and about 2.5km from the seashore.

The Eastern Mediterranean region is characterized by air masses arriving from different sources (Lelieveld et al., 2002). Many of these air masses often contain aerosols from distant and local anthropogenic sources (Levin and Lindberg, 1979; Graham et al., 2004). Some contain dust particles from the Sahara desert (Ganor, 1994; Levin et al., 2005) while others contain marine and biogenic aerosols from the Mediterranean Sea (Levin et al., 1990) and from land sources (Ganor et al., 2000). In some cases the desert dust particles undergo changes due to chemical processes (e.g. sulfate coating; Levin et al., 1996) and/or attachment to other particles such as sea salt (Levin et al., 2005).

Air masses reaching Tel Aviv from the northwest carry a larger fraction of marine aerosols, mainly sea spray and anthropogenic aerosols with a relatively small fraction of desert particles. Air masses reaching the measuring station from the southwest (Sahara and North African deserts), carry a larger fraction of desert and marine aerosols with a smaller fraction of

anthropogenic particles (Levin et al., 1990, 2005). Dust also reaches Israel from the east, although dust storms from the North African (southwest) deserts are more common with much lower visibility and much higher aerosol loading (Ganor et al., 1991). Ganor and Foner (1996) showed that the chemical composition of dust transported from North Africa is similar to the dust transported from the east direction. Both dust sources contain soluble and insoluble inorganic material as well as organic matter, but they are distinguished by their clay mineralogy. These desert aerosols are mainly composed of quartz, calcite, dolomite, feldspars, gypsum and clay minerals (Ganor and Mamane, 1982). Ganor (1994) found an average of 19 dust storms per year based on 33 years of observations. Dust storms are most common between December and April (Katznelson, 1970) with maxima occurrences in spring time, mainly during April (Ganor, 1994). During the summer very few dust storms occur (Ganor et al., 1991). Although during dust storms mineral dust particles are present in high concentrations, such dust aerosols are almost always present in the atmosphere in this region (Levin and Lindberg, 1979).

Every year for one day during the month of May the Eastern Mediterranean area is filled with biomass burning particles due to the Lag BaOmer (LBO) event. LBO is a national Israeli holiday where many people set bonfires in open spaces around the country. The event starts usually at sunset (around 19:00 local time) and lasts throughout most of the night (usually until sunrise). Most of the bonfires burn dry processed Finish Pine wood taken from construction sites. Often the heavy smoke is generated from low temperature smoldering combustion, which would be classified as type A (extinguishable by water; Boothroyd, 2005). The high level of pollution due to these fires can be detected from satellites (Kaufman et al., 2006). LBO events have been studied in the past (e.g. Sarnat et al., 2010; von Schneidemsser et al., 2010) including studies of the particles' chemical aging and optical properties (e.g. Adler et al., 2011). However, no studies have been reported on the properties of these particles as ice nuclei.

3 Method of analysis

A total of 19 filter samples were collected during Jan 2009 to Dec 2010. The aerosols were sampled for twenty minutes on Nitrocellulose Membrane Black filters of 47mm diameter and 0.45μm pore size which were held in a standard Millipore open metal holder type with flow rate of 20 LPM (total of 400L on each filter). The open inlet of the filter holder was facing down,

with the holder itself being held at a distance of one and a half meters from the floor. Table 1 presents a list of the filters that were sampled during days which were classified (see below the classification criteria for each case) as dust storms, clean and polluted days (e.g LBO) and days which did not fit either the dust storm or clean conditions.

The aerosol total concentration was measured by TSI Condensation Particle Counter (CPC) Model 3010, which was located next to the filter sampler. In order to measure the concentration of particles in the size range of 0.11-3μm, a TSI Particle Size Selector Model 376060 with a number of screens placed in the front, were used to remove particles smaller than 0.112 microns. With this instrument the total number concentration (Nt) of the aerosols in this size range was measured and used to calculate the activated fraction (AF) values of the freezing nuclei (#IN/Nt). In addition, at the beginning of the measurement period in Jan 2009 and for a relatively short time afterwards, a Passive Cavity Aerosol Spectrometer Probe 100X (PCASP-100X) was used on a daily basis to measure aerosol size distributions in the range 0.1 to 3 μm.

Aerosol mass concentration of PM_{10} and $PM_{2.5}$ (Particulate Matter with aerodynamic diameter of less than 10μm and 2.5μm, respectively) were also used. These data were downloaded from the website of the Ministry of Environmental Protection (http://www.svivaaqm.net/Default.rtl.aspx). The PM_{10} data was taken from the Yad Avner Station (32°7'9.4"N 34°48'17.9"E) located about 700m north of the sampling station. The $PM_{2.5}$ data was taken from a station at the Municipal High School Ironi D Station (32°5'34.9"N 34°47'27.5"E) located about 2.5km south west of the sampling site. Aerosol number concentration and aerosol mass concentration (PM_{10} and $PM_{2.5}$) are also listed in Table 1.

The immersion freezing measurements were conducted using the FRIDGE-TAU (FRankfurt Ice-nuclei Deposition freezinG Experiment, the Tel Aviv University version) chamber (See Fig. 2 in Ardon-Dryer et al., 2011). This chamber, which is usually used for studying ice formation by deposition and by condensation freezing (Bundke et al., 2008; Klein et al., 2010b), was used here to determine the temperature at which freezing of drops containing aerosols took place.

Each filter containing the collected aerosols was placed in 10ml of double distilled water (resistivity of 18.2 MΩ·cm). The aerosols were then removed from the filter by an ultrasonic shaker. The use of the ultrasonic shaker was found to be effective for particle removal into the water solution. This method which is more aggressive then the removal method used by Vali

(1968) was found to be effective in removing all of the most effective particles after only one cycle of shaking in the ultrasonic bath. The resulting mixture of water and aerosols was the source of the drops tested for immersion freezing. Each test consisted of about 140 drops (1μl; 0.8mm diameter) placed by a pipette on the temperature controlled stage of the FRIDGE-TAU. A thin layer of Vaseline was first put on the stage in order to prevent ice from forming on the surface during cooling. This was necessary to prevent the formation of very thin ice dendrites which grow by vapor deposition from the perimeter of some frozen drops, reaching and freezing some of their neighbors, thus affecting the measurements. The temperature of the cooling stage was lowered at a constant rate of 1°C min^{-1} and the number of drops that froze at each temperature was recorded by a CCD (Charge-Coupled Device) camera.

In most cases the filters were cut in half before placing them in 10 ml of double distilled water. This was done in order to be able to duplicate the measurements if needed. In some cases the unused half of the filter was used for elemental analysis of individual particles with the Environmental Scanning Electron Microscope (ESEM) with an attached X-ray energy dispersive system (EDS). The exceptions were the filters from the 24 Jan 2009, 19 Feb 2009 and 17 Dec 2009 which were not cut and were immersed in the distilled water and in the ultrasonic shaker.

3.1 Calculation of immersion-freezing nuclei (FN) concentration

In order to estimate the concentrations of immersion freezing nuclei (FN) in the air we converted Vali's (1971) equation taking into account the amount of air that had been sampled in each measurement. The equation is composed of two parts: the first is an integration of the differential probability that a drop will freeze at temperatures between T and $T-\Delta T$ due to the presence of a single active nucleus in it over the temperature range from 0ºC to T. The result of the integration is the cumulative nucleus concentration K'(T), which represents the number of nuclei active at all temperatures warmer than T. In order to obtain the actual concentrations of ice nuclei in the sampled air, consideration must be given to the total air sampled. This is presented in the last part of the equation:

$$K'(T) = \frac{1}{V} \times \left[\ln(N_0) - \ln(N(T))\right] \times \frac{x}{y} \quad (1)$$

K'(T) - Cumulative concentration of FN in the air active at temperature T (L^{-1})

V - Volume of drop (L)

No - Total number of drops measured

N (T) - Number of unfrozen drops at temperature T

x - The volume of water used to remove the aerosols from the filter (L)

y - The volume of air sampled through the filter (L)

Equation (1) was verified and found to be a reliable equation based on laboratory measurements of montmorillonite particles (SWy-2 Na-Montmorillonite) on one filter. Three experiments were made with the same filter in which we diluted the aerosols in the sample three successive times and analyzed them each time in immersion freezing mode. The dilution was done by placing the filter in the test tube and removing the aerosols into 5ml of doubly distilled water. Drops from this sample were analyzed in the immersion freezing mode. Then another 5ml of water was added (total of 10ml without extra shaking) and drops from this mixture were analyzed. Finally 40ml of water were added to the same tube (total of 50ml without extra shaking) followed by analysis of drop freezing. The cumulative freezing spectra of the three experiments are shown in Fig. 2. As expected, the more diluted the sample, the bigger is the shift of the cumulative spectrum to lower temperatures. The reason for this is that the dilution decreases the probability that a good IN will be present in the drop. However, converting these cumulative results to FN concentrations in the air based on Eq. (1) gives very similar concentrations. The montmorillonite onset freezing temperature (the temperature at which the first drop freezes) were similar to the onset freezing temperature of Zimmermann et al. (2008), Hoffer (1961) and Salam et al. (2007).

4 Results and discussion

Nineteen filters from different days were sampled under different conditions, as can be seen in Table 1. A total of 2720 drops were analyzed. All drops, regardless of the sample used, froze between -11.8ºC to -28.9ºC, with median freezing that varied from -17.8ºC down to -24.4ºC, as can be seen from Table. 2. The freezing of all drops from the sampled filters occurred at warmer temperatures as compared to water drops taken from pure water, or those taken from the blank filters. It should be noted however, that a small overlap between the blank filters and the sampled

ones was observed at temperatures between -23ºC to -29ºC. The overlap amounted to a total of 196 droplets comprising 7.2% of the total drop population. This means that about 7.2% of the drops could freeze at these temperatures even in the absence of aerosols. Therefore, in the following analysis, the fraction of drops from the sampled filters that froze at the same temperature as the blank have been removed. The effect of the reduction on the calculated concentrations was small, from 0.1% to 11.4% over the temperature range in the experiment. After the subtraction of these drops, the median temperature shifted by an average of 0.18ºC.

The drops containing the collected ambient particles began to freeze at lower temperatures than those reported from some biological aerosols such as bacteria and leaf litters (e.g. Schnell and Vali, 1976; Maki and Willoughby, 1978; Schnell et al., 1982; Levin and Yankofsky, 1983). The freezing spectra were found to be warmer than those reported by Ardon-Dryer et al. (2011) for the South Pole. Most onset freezing temperatures in this work were lower than those measured by Conen et al. (2012) in the High Alpine Research Station Jungfraujoch in the Swiss Alps. It is interesting to point out that Kanitz et al. (2011) and Seifert et al. (2010) observed a relatively high fraction of ice in mid-level startiform clouds with cloud top temperatures as warm as -10ºC or even warmer when dust particles were present. This is very similar to the results of Levin et al. (1996) who reported on ice concentrations in Eastern Mediterranean convective clouds. It is also in good agreement with the present results showing the effectiveness of the mineral dust particles as freezing nuclei at such warm temperatures.

The median freezing temperatures of the droplets in each case were found to be correlated with the corresponding daily average values of PM_{10}, $PM_{2.5}$ and PM_{10}-$PM_{2.5}$ (see Fig. 3). The correlation value of $PM_{2.5}$ (R^2=0.42) was lower than those measured for PM_{10} and PM_{10}-$PM_{2.5}$ (R^2=0.47). This suggests that the more effective freezing nucleation is associated with the larger particles, those that fall into the range PM_{10}-$PM_{2.5}$ Furthermore, as the aerosol concentration increased, the median freezing temperatures of the droplets was higher. These results are in agreement with many other reports (e.g. Garten and Head, 1964; Philips et al., 2008; Welti et al., 2009; Klein et al., 2010b; Niedermeier et al., 2011) showing the correlation between ice nuclei concentrations and the surface area of the particles.

The FN concentration of all the samples was calculated based on Eq. (1). The FN concentration varied from $0.16L^{-1}$ to $234L^{-1}$, as can be seen in Fig. 4. As expected, the concentration of active

nuclei increases as the temperature decreases. Calculating the best fit line (black line in Fig. 4) from the entire data results in an exponential equation;

$$N_{FN} = 3\times10^{-4} e^{0.53\Delta T} \quad (2)$$

Where N_{FN} represents the concentrations of FN (L^{-1}) and ΔT represents the supercooling in ºC With this equation a concentration of $1L^{-1}$ is reached at -15.3ºC. This temperature is higher than the average temperature obtained by Bigg and Stevenson's (1970) measurements of condensation freezing that were taken around the world. These measurements are also higher than the condensation freezing measurements of Gagin (1975) that were observed in Israel (~$1L^{-1}$ at -18.4ºC).

Activated fraction (AF) values of all the filters were also calculated based on the total aerosol concentration (Nt) in the size range of 0.11-3µm, which were measured simultaneously with the filters. The average AF value of all the filters was $4.9x10^{-5}$ ± $8.1x10^{-5}$ (average ± standard deviation value) with variations from $8.7x10^{-8}$ to $4.9x10^{-4}$, as can be seen in Fig. 5. All the activated fraction values were combined and a best fit line was calculated (see black line in Fig. 5). The majority of AF values were in the range of values (10^{-3}-10^{-6}, for particle >0.1µm) proposed by Pruppacher and Klett (1997) However, the lowest AF value was much lower than in Pruppacher and Klett's (1997).

The concentration of FN and the values of AF increased as the temperatures decreased; the relatively high correlation values (>0.65) imply a strong dependence of FN on temperature. Similar dependence was observed in many previous publications (e.g. Meyers et al., 1992; Vali, 2008; Niedermeier et al., 2010). It is important to note that the lack of a clear temperature dependence of ice crystal concentrations in clouds (Gultepe et al, 2001) suggests that other parameters such as the chemistry of the aerosols, their surface area (Philips et al., 2008) and the concentration of aerosols larger than 0.5µm (DeMott et al., 2010) also play an important role in the nucleation.

4.1 Immersion-Freezing Nuclei during dust storms and clean conditions.

The filter samples were separated into dust storms and clean conditions based on PM_{10} values and the air mass back trajectory. The Back Trajectories (BT) were calculated for each measurement using the HYSPLIT method (Hybrid Single Particle Lagrangian Integrated Trajectory Model). Dust storm days were defined as days when the PM_{10} daily average values and the value measured during the aerosol sampling time exceeded 100μg m^{-3} (Ganor et al., 2009). In addition, the air mass trajectory in the previous 72 hours had to have originated over a dust source or passed over one. Samples were defined as clean days when PM_{10} daily average values and the value measured during the aerosol sampling were below 50 μg m^{-3} (Ganor et al., 2009) and the air mass trajectory in the previous 72 hours did not pass over a source of dust. It should be noted that in the research area the yearly average standard values of PM_{10} is 60μg m^{-3} (Israel Ministry of Environmental Protection, 2013).

Out of all the days that were sampled, eight days were defined as dust storm days with daily average values of PM_{10} from 254 to 867μg m^{-3}, with an overall average of 527±236. Five days were defined as clean days, with PM_{10} daily averages ranging from 30 to 39μg m^{-3} with an overall average of 34±3.8, as can be seen in Table 3. In the clean cases the air mass arrived from the west or northwest, while on the dust storms days the air mass arrived from the south or southwest, as can be seen in Fig. 6.

Determinations of FN and AF during dust storm days were based on a total of 1173 droplets while the clean days were based on 626 droplets. The onset of drop freezing of samples from the dust storm days started at -11.8°C and freezing continued until -25.1°C, while for the clean days onset of drop freezing started at temperature -15.3°C and the last drop froze at -27.4°C, as can be seen in Table 3. The median freezing temperature of the dust storm days occurred at 1.8 degree warmer compared to the clean days. Significant statistical difference (based on T test) was found between the dust storm and the clean conditions in term of onset of drop freezing, the median freezing temperatures and the aerosol mass loading (PM's).

FN concentrations (Fig. 7A) and AF values (Fig. 7B) were calculated separately for the clean and dust storm conditions. FN concentrations in dust storms ranged from $0.16L^{-1}$ up to $218L^{-1}$ while the AF values ranged from $8.7x10^{-8}$ up to $4.9x10^{-4}$. In the clean conditions FN concentrations ranged from $0.4L^{-1}$ to $222L^{-1}$ with the corresponding AF values ranging from

$2.1x10^{-7}$ to $4.9x10^{-4}$. Best-fit lines representing dust storm and clean conditions were calculated. Fig. 7 demonstrates that the FN concentrations and AF values of the dust storm days were higher by more than a factor of 2 as compared with the clean days. Similar increases were found by Levi and Rosenfeld (1996) in their measurements in the same region. It is interesting to point out that the differences between clean and dust storm conditions in regions where dust is not so common, such as Florida and Central Europe, are much greater (DeMott et al., 2003a; Klein et al., 2010b). The relatively small increase in FN concentrations and AF values that were found between the clean and dust storm conditions led us to investigate whether there is a difference (in FN concentrations and AF values) between the two conditions. FN concentrations and AF values in the dust storm and clean conditions did not show a significant statistical difference (based on T test). This suggests that dust particles are always present in the Eastern Mediterranean atmosphere even on days without dust storms, as was found by Levin and Lindberg (1979).

Single particle analyses using the Environmental Scanning Electron Microscope (ESEM) with an attached X-ray energy dispersive system (EDS) were performed on two samples collected on filters during two days (May 27 2010 and Nov 15 2010). A total of 203 particles were analyzed, and the frequency of occurrence of the different elements is presented in Table 4. The air mass trajectories on these two days originated from dust sources, thus the presence of dust particles was expected. Ca was the most abundant element and it was found in most of the particles (>90%). Al, Si and Fe were found in somewhat fewer particles (>50%). According to Falkovich et al. (2001), mineral dust particles in the Eastern Mediterranean contain Si, Al, Mg, K, Ca and Fe. Out of all the particles that were analyzed, 28% contained all these elements. Some of the dust particles also contained sulfate and NaCl. The presence of sulfate and sea salt on dust particles have been reported in the past by Levin et al. (1996) and Levin et al. (2005), respectively. Many particles (48% of the particles from Nov 15 2010) were identified as Calcite minerals. Some of the particles (4%) contained Ca together with S, suggesting the presence of gypsum (Levin and Lindberg, 1979; Levin et al., 1996). Such combination could also originate from a mixture of dust with anthropogenic pollution according to Graham et al. (2004). A few of the particles were identified as clay mineral (montmorillonite and illite) and a few others as Feldspars. These findings are in agreements with those of Ganor (1991) and Ganor et al. (2009)

who found montmorillonite, calcite, gypsum, illite and feldspar in particles from dust storms in the Eastern Mediterranean area.

Fig. 7 also shows a comparison of FN concentration from dust storms and clean conditions and the measurements of ice nucleation by condensation freezing taken in the same research area by Levi and Rosenfeld (1996) and Gagin (1975). The figure shows some agreement between the two modes of nucleation at the higher temperatures while there are differences of about one order of magnitude at lower temperatures. One possible explanation for this difference is that immersion freezing is more effective than condensation freezing. On the other hand, it is also possible that the difference is a result of the measuring method.

In order to compare the present results with results from laboratory studies, there was a need to calculate the ice nucleation active surface site (INAS) densities, (e.g Hoose and Möhler, 2012; Murray et al., 2012 and references therein).

4.1.1 Calculation of ice nucleation active surface site (INAS) densities

In order to calculate the INAS densities, measurements of size distributions were needed. In addition, to the total aerosol concentration that were measured in the size range of 0.11 to 3μm by the CPC, at the beginning of the measurement period in Jan 2009 and for a relatively short time afterwards, a PCASP-100X was used on a daily basis to measure aerosol size distributions in the range 0.1 to 3μm. Due to instrumental difficulties, data from the PCASP were obtained in only four days, defined as clean cases and only three days that were classified as dust storms days.

Fig. 8 presents the average size distribution on the dust storm days as well as the average size distribution on the clean days. From these measurements the average total particle concentration in the size range of 0.5-3μm for the clean cases was 2±1 cm^{-3} while for dust storm cases it was 21±9 cm^{-3}. For comparison, the figure presents the present results superimposed on the distributions of dust reported by Levin et al. (1980). Out of these seven days only two filter samples in dust storms events (15 and 19 February, 2009) were collected simultaneously by the

CPC and the PCASP measurements. It is clear that our measured distributions in the dust storms cases are very similar to those measured many years ago in the eastern Mediterranean and in other locations.

Due to the fact that the size distributions on the three dust storm days were very similar to each other and also similar to the other dust storms that were measured in the past, it was decided to use the ratio of the data from the PCASP and the CPC as a scaling factor to estimate the size distribution on days in which no data from the PCASP was available.

The following ratio was calculated to provide a scaling factor between the CPC and PCASP total counts:

$$\overline{X}_{dust} = Nt_{(PCASP\ 0.11-3)}/Nt_{(CPC\ 0.11-3)} \quad (3)$$

Then we calculated the fraction of particles in the 0.5 to 3 μm in the PCASP measurements:

$$\overline{Y}_{dust} = Nt_{(PCASP\ 0.5-3)}/Nt_{(PCASP\ 0.11-3)} \quad (4)$$

The average number of particles per size from the days in which the PCASP data is available is given by:

$$\overline{Z}_{i(PCASP\ 0.5-3)} = \frac{n_i}{N_{T\_(PCASP\ 0.5-3)}} \quad (5)$$

Based on these scaling factors one can estimate the number of particles in each size on days when only the CPC data were available:

$$n_i^* = \overline{X}_{dust} * \overline{Y}_{dust} * \overline{Z}_{i(PCASP\ 0.5-3)} * N^*_{T\_CPC} \quad (6)$$

Where n_i^* is aerosol number concentration per size i on days when no PCASP data were available. $N^*_{T\_CPC}$ is the total aerosol number concentrations (cm^{-3}) measured by the CPC. The same procedure was not followed for the clean days because the size distribution on the days that PCASP data were available varied greatly, with some days having larger particles present while in others much narrower distributions were measured.

With these calculated size distributions the ice nucleation active surface site (INAS) densities were calculated. The INAS density describes the number of ice nucleation active sites at a certain temperature and supersaturation, normalized by the aerosol surface area. Due to the fact that this experiment was carried out in the immersion freezing mode, the calculations were done

assuming the nucleation occurred under water saturation. The INAS was calculated using the method proposed by Hoose and Möhler (2012):

$$n_s(T) = -1/A_{aer} * ln(1 - f_{IN}(T)) \quad (7)$$

Where $f_{IN,}$ is the ice nucleation active fraction under the considered conditions. In our case the activated fraction was calculated for particles larger than 0.5μm as measured by the PCASP or scaled by the method above. A_{aer} is the aerosol surface per particle, which is equal to the total surface area of all the aerosols (assuming they are spherical particles) divided by the total aerosol number concentration.

INAS density values for the dust storm cases range from $1.1x10^5$ to $4.9x10^9$, as can be seen in Fig. 9. The results from the immersion freezing in this work fall well within the range of measurements presented by Hoose and Möhler (2012). The steep increase in INAS density values with lowering of temperature (Fig. 9) agrees well with the results of Connolly et al. (2009), Niedermeier et al. (2010) and Murray et al. (2011), who compared the values of INAS of different mineral dusts in the laboratory. It is interesting to point out that one dust sample that was measured by Niedermeier was a sample of Israeli dust (see Fig. 9).

4.2 The Lag BaOmer bonfires

On May 01, 2010 we had an opportunity to sample the FN concentration during the Lag BaOmer (LBO) holiday. Aerosols for freezing nuclei measurements were sampled a few hours before the start of the LBO bonfires (15:00 local time) and during the event itself (May 01, 2010 23:00 local time). The smell of smoke was present in the air even though the sampling station was a few kilometers away from any bonfires. The total particle concentration in addition to PM_{10} and $PM_{10-2.5}$ values increased during the time that the bonfires were lit. This can be seen in Fig. 10 where PM_{10}, $PM_{10-2.5}$ and total particle concentrations are presented. It is important to note that these low temperature fires produced high concentrations of particles many of which were larger than 2.5μm as can be seen in the values of $PM_{10-2.5}$.

The effectiveness of biomass burning in producing ice nuclei concentrations has been studied by a number of groups in the past. However, a wide range of results about the effectiveness of these particles as ice nuclei can be found in the literature. For example, Hobbs and Locatelli (1969)

measured downwind of a natural forest fire in Stampede Pass in the state of Washington. These fires burn Lodgepole Pine and White Pine and produce heavy smoke with high concentrations of ice nuclei. Similarly, Pratt et al. (2011) who measured smoke from mountain sagebrush plumes in Wyoming observed significant increases in ice nuclei concentrations. On the other hand, some reports show that certain types of fires such as smoldering combustion produce particles that are not as effective as ice nuclei (Prenni et al., 2012). Petters et al. (2009) concluded that emissions from fires with low organic carbon fraction, high water-soluble ion content and high burning temperatures are associated with a larger amount of ice nuclei. Since most of the wood type used in the LBO fires is different from the ones studied before, it was interesting to study its effectiveness as a source of ice nuclei.

We observed that the temperature at which the particles nucleated ice, the activated fraction and the freezing nuclei concentrations before the LBO bonfires (15:00 local time) were higher as compared to those measured during the event itself (23:00 local time). For example, $1L^{-1}$ was observed before LBO at -16.5ºC, 1.5ºC warmer than the one measured during the fires themselves (as can be seen in Fig. 4). The activated fractions over the whole temperature range before LBO was about four times higher than during the holiday bonfires. In summary, our measurements agree with the conclusions of Petters et al. (2009) that the low concentration of ice nuclei during the LBO event is due to the combination of the relatively low temperatures of the fires and the high organic carbon fraction in the fires as was measured by Adler et al. (2011). In summary, although the bonfires on LBO produced numerous particles, their effectiveness as freezing nuclei is relatively poor.

5 Conclusions

Immersion Freezing Nuclei were measured from samples collected on different days in Israel during Jan 2009 to Dec 2010. Drops containing ambient aerosols were found to freeze between -11.8ºC down to -28.9ºC, with median freezing temperature that varied from -17.8ºC down to -24.4ºC. FN concentrations range between $0.16L^{-1}$ to $234L^{-1}$ while the activated fraction ranges between $8.7x10^{-8}$ to $4.9x10^{-4}$. The median temperature at which the drops from each filter froze were found to be correlated with the corresponding daily average of PM_{10}, $PM_{2.5}$ and PM_{10}-$PM_{2.5}$. The fact that the correlation value between FN concentrations and PM_{10}-$PM_{2.5}$ was higher

than $PM_{2.5}$ suggests that the larger particles are generally more effective as FN. This is in agreement with the notion that the activity of ice nucleation is correlated with surface area.

Classification of part of the samples into dust storm and clean conditions based on their back trajectory and aerosol mass concentrations (PM_{10}) was done. Droplets containing ambient particles from dust storm days froze at warmer temperatures than droplets containing particles from clean days. The difference between the clean and dust storm days was significant statistically in term of onset of drop freezing temperature, median freezing temperature and aerosol concentration (PM's). FN concentrations and AF values in dust storms were larger by more than a factor of two than in the clean conditions. This observation agrees with previous studies showing that some dust particles are almost always present in the atmosphere in this region.

It was observed that although the bonfires during the Lag BaOmer holiday produce high concentrations of aerosols, their effectiveness as freezing nuclei was relatively poor. The reason for this stems from the relatively low fire temperatures and high organic carbon fraction in the aerosols.

Acknowledgements

We would like to acknowledge the German Israeli Foundation (GIF) grant number 1-860-27 for their support and Dr. Heinz Bingemer, Dr. Holger Klein, Dr. Ulrich Bundke, Werner Haunold, Robert Sitalh, Anja Danielczokand and Jann Schrod from the Institute for Atmospheric and Environmental Sciences, Goethe-University, Frankfurt, Germany for all the help and support with the FRIDGE-TAU chamber. Thanks are due to the students Israel Silver and Roy Jaijel from Tel Aviv University and to Sarvesh Garimella from MIT for their help with the sampling and the analysis.

We want to thank the reviewer Paul DeMott and two anonymous reviewers for their very constructive comments, which helped improve the paper. In addition, thanks are due to Prof. Gabor Vali and to Dr. P. Seifert for their comments.

References

Adler, G., Flores, J. M., Abo Riziq, A., Borrmann, S., and Rudich, Y.: Chemical, physical, and optical evolution of biomass burning aerosols: a case study, Atmos. Chem. Phys., 11, 1491-1503, doi:10.5194/acp-11-1491-2011, 2011.

Ardon-Dryer, K., Levin, Z., and Lawson, R. P.: Characteristics of immersion freezing nuclei at the South Pole station in Antarctica, Atmos. Chem. Phys., 11, 4015-4024, doi:10.5194/acp-11-4015-2011,2011.

Bigg, E. K. and Stevenson, C. M.: Comparison of ice nuclei in different parts of the world, J. Rech. Atmos., 4, 41-58, 1970.

Broadley, S. L., Murray, B. J., Herbert, R. J., Atkinson, J. D., Dobbie, S., Malkin, T. L., Condliffe, E., and Neve, L.: Immersion mode heterogeneous ice nucleation by an illite rich powder representative of atmospheric mineral dust, Atmos. Chem. Phys., 12, 287-307, doi:10.5194/acp-12-287-2012, 2012.

Boothroyd, T.: Fire Detection and Suppression Systems, Intl Fire Service Training Assn, USA, 2005.

Bowdle, D. A., Hobbs, P. V., and Radke, L. F.: Particles in the Lower Troposphere over the High Plains of the United States. Part III: Ice Nuclei, J. Climate Appl. Meteor., 24, 1370-1376, 1985.

Bundke, U., Nillius, B., Jaenicke, R., Wetter, T., Klein, H., and Bingemer, H.: The fast ice nucleus chamber FINCH, Atmos. Res., 90, 180-186, 2008.

Chou, C., Stetzer, O., Weingartner, E., Juranyi, Z., Kanji, Z. A., and Lohmann, U.: Ice Nuclei Properties within a Saharan dust event at the Jungfraujoch in the Swiss Alps, Atmos. Chem. Phys., 11, 4725-4738, doi:10.5194/acp-11-4725-2011, 2011.

Conen, F., Henne, S., Morris, C. E., and Alewell, C.: Atmospheric ice nucleators active ≥-12 °C can be quantified on PM_{10} filters, Atmos. Meas. Tech., 5, 321-327, doi:10.5194/amt-5-321-2012, 2012.

Connolly, P. J., Möhler, O., Field, P. R., Saathoff, H., Burgess, R., Choularton, T., and Gallagher, M.: Studies of heterogeneous freezing by three different desert dust samples, Atmos. Chem. Phys., 9, 2805–2824, doi:10.5194/acp-9-2805-2009, 2009.

Cziczo, D. J., DeMott, P. J., Brock, C. A., Hudson, P. K., Jesse, B., Kreidenweis, S. M., Prenni, A. J., Schreiner, J., Thomson D. S., and Murphy D. M.: A method for single particle mass spectrometry of ice nuclei, Aerosol. Sci. Tech., 37, 460-470, 2003.

Cziczo, D. J., Thomson, D. S., Thompson, T. L., DeMott P. J., and Murphy D. M.: Particle analysis by laser mass spectrometry (PALMS) studies of ice nuclei and other low number density particles, Int. J. Mass Spectrom., 258, 21-29, 2006.

Cziczo, D.J. Froyd, K.D. Hoose, C. Jensen, E.J. Diao, M. Zondlo, M.A. Smith, J.B Twohy, C.H., and Murphy, D.M: Clarifying the Dominant Forces and Mechanisms of Cirrus Cloud Formation, Science., 340, 1320-1324, 2013.

DeMott, P. J., Sassen, K., Poellet, M. R., Baumgardner, D., Rogers, D. C., Brooks, S. D., Prenni, A. J., and Kreidenweis, S. M.: African dust aerosols as atmospheric ice nuclei, Geophys. Res. Lett., 30, 1732, doi:10.1029/2003GL017410, 2003a.

DeMott, P. J, Cziczo, D., Prenni, A., Murphy, D., Kreidenweis, S., Thomson, D., Borys, R., and Rogers, D.: Measurements of the concentration and composition of nuclei for cirrus formation, Proc. Nat. Acad. Sci., 100, 14 655-14 660, 2003b.

DeMott, P. J., Prenni, A. J., Liu, X., Kreidenweis, S. M., Petters, M. D., Twohy, C. H., Richardson, M. S., Eidhammer, T., and Rogers D. C.: Predicting global atmospheric ice nuclei distributions and their impacts on climate, Proc. Natl. Acad. Sci. USA., 107, 11217-11222, 2010.

DeMott, P. J., Möhler, O., Stetzer, O., Vali, G., Levin, Z., Petters, M. D., Murakami, M., Leisner, Th., Bundke, U., Klein, H., Kanji, Z. A., Cotton, R., Jones, H., Benz, S., Brinkmann, M., Rzesanke, D., Saathoff, H., Nicolet, M., Saito, A., Nillius, B., Bingemer, H., Abbatt, J. P. D., Ardon, K., Ganor, E., Georgakopoulos, D. G., and Saunders, C.: Resurgence in ice nuclei measurement research, Bull Amer Meteor Soc., 92(12), 1623-1635, doi:10.1175/2011BAMS3119.1, 2011.

Diehl, K., Matthias-Maser, S., Jaenicke, R., and Mitra, S. K.: The ice nucleating ability of pollen: Part II. Laboratory studies in immersion and contact freezing modes, Atmos. Res., 61, 125–133, 2002.

Falkovich, A., Ganor, E., Levin, Z., Formenti P., and Rudich, Y.: Chemical and mineralogical analysis of individual mineral dust particles, J. Geophys. Res., 106, 18029-18036, 2001.

Froyd, K. D., Murphy, D. M., Lawson, P., Baumgardner, D., and Herman, R. L.: Aerosols that form subvisible cirrus at the tropical tropopause, Atmos. Chem. Phys., 10, 209-218, doi:10.5194/acp-10-209-2010, 2010.

Gagin, A.: The Ice Phase in Winter Continental Cumulus Clouds, J. Atmos. Sci., 32, 1604-1614, 1975.

Ganor, E.: The Frequency of Saharan Dust episodes over Tel-Aviv, Israel, Atmos. Environ., 28, 2867-2871, 1994.

Ganor, E. and Foner, H.: The mineralogical and chemical properties and the behavior of the aeolian Saharan dust over Israel, in: The Impact of Desert Dust Across the Mediterranean, Guerzoni S. and Chester R. (Ed), Kluwer Academic Publishers, Netherlands, 163-172, 1996.

Ganor, E. and Mamane, Y.: Transport of Saharan dust across the eastern Mediterranean, Atmos. Envir., 16, 581-587, 1982.

Ganor, E., Foner, H. A., Brenner, S., Neeman, E., and Lavi, N.: The chemical composition of aerosols settling in Israel following dust storm, Atmos. Envir., 25A, 2665-2670, 1991.

Ganor, E., Foner, H. A., Bingemer, H. G., Udiste, R., and Setter, I.: Biogenic sulfate generation in the Mediterranean Sea and its contribution to the sulfate anomaly in the aerosol over Israel and eastern Mediterranean, Atmos. Envir., 34, 3453-3462, 2000.

Ganor, E., Stupp, A., and Alpert, P.: A method to determine the effect of mineral dust aerosols on air quality, Atmos. Envir., 43, 5463-5468, 2009.

Garten, V. A. and Head, R. B.: Carbon Particles and Ice Nucleation, Nature, 201, 1091-1092, 1964.

Google map: https://maps.google.com/ (last access: 10 November 2012), 2012.

Goudie, A. S. and Middleton, N. J.: Desert Dust in the Global System, Springer Berlin Heidelberg, New York, 2006.

Graham, B., Falkovich, A. H., Rudich, Y., Maenhaut, W., Guyon, P., and Andreae, M. O.: Local and regional contributions to the atmospheric aerosol over Tel Aviv, Israel: a case study using elemental, ionic and organic tracers, Atmos. Envir., 38 1593-1604, 2004.

Gultepe, I., Isaac, G. A., and Cober, S. G.: Ice crystal number concentration versus temperature for climate studies, Internat. J. Climatology., 21, 1281-1302, 2001.

Hobbs, P. V. and Locatelli, J. D.: Ice nuclei from a natural forest fire, J. Appl. Meteor., 8, 833-834, 1969.

Hoffer, T.: A laboratory investigation of droplet freezing, J. Met., 18, 766-778, 1961.

Hoose, C., Kristjánsson, J. E., and Burrows, S. M.: How important is biological ice nucleation in clouds on a global scale? Environ. Res. Lett., doi:10.1088/1748-9326/5/2/024009 5, 1-7, 2010.

Hoose, C. and Möhler, O.: Heterogeneous ice nucleation on atmospheric aerosols: a review of results from laboratory experiments, Atmos. Chem. Phys., 12, 9817-9854, doi:10.5194/acp-12-9817-2012, 2012.

IPCC, Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Paris, 2007.

Isono, K.: On ice crystal nuclei and other substances found in snow crystals, J. Meteor., 12, 456-462, 1955.

Isono, K., Komabayasi, M., Takeda, T., Tanaka, T., Iwai, K., and Fujiwara M.: Concentration and nature of ice nuclei in rim of the North Pacific Ocean, Tellus, 23, 40-59, 1971.

Israel Ministry of Environmental Protection, http:// http://www.sviva.gov.il/subjectsEnv/SvivaAir/Laws/Pages/toxicityvalue.aspx (last access: 10 May 2013), 2013 (in Hebrew).

Kanitz, T., Seifert, P., Ansmann, A., Engelmann, R., Althausen, D., Casiccia, C., and Rohwer, E. G.: Contrasting the impact of aerosols at northern and southern midlatitudes on heterogeneous ice formation, Geophys. Res. Lett., 38, L17802, doi:10.1029/2011GL048532. 2011.

Kanji, Z. A., DeMott, P. J., Möhler, O., and Abbatt, J. P. D.: Results from the University of Toronto continuous flow diffusion chamber at ICIS 2007: instrument intercomparison and ice onsets for different aerosol types, Atmos. Chem. Phys., 11, 31-41, doi:10.5194/acp-11-31-2011, 2011.

Kanji, Z. A., Welti, A., Chou, C., Stetzer, O., and Lohmann, U.: Laboratory studies of immersion and deposition mode ice nucleation of ozone aged mineral dust particles, Atmos. Chem. Phys., 13, 9097-9118, doi:10.5194/acp-13-9097-2013, 2013.

Katznelson, J.: Frequency of dust storms at Be'er Sheva, Israel, J. Earth Sci., 19, 69-76, 1970.

Kaufman, Y. J., Gobbi, G. P., and Koren, I.: Aerosol climatology using a tunable spectral variability cloud screening of AERONET data, Geophys. Res. Lett., 33, L07817, doi: 10.1029/2005GL025478, 2006.

Klein, H., Nickovic, S., Haunold, W., Bundke, U., Nillius, B., Ebert, M., Weinbruch, S., Schütz, L., Levin, Z., Barrie, L. A., and Bingemer, H.: Saharan dust and ice nuclei over Central Europe, Atmos. Chem. and Phys., 10, 10211-10221, doi:10.5194/acp-10-10211-2010, 2010a.

Klein, H., Haunold, W., Bundke, U., Nillius, B., Wetter, T., Schallenberg, S., and Bingemer, H.: A new method for sampling of atmospheric ice nuclei with subsequent analysis in a static diffusion chamber, Atmos. Res., 96, 218-224, 2010b.

Kulkarni, G. and Dobbie, J.: Ice nucleation properties of mineral dust particles: determination of onset RHi, IN active fraction, nucleation time-lag, and the effect of active sites on contact angles, Atmos. Chem. and Phys., 10, 95-105, doi:10.5194/acp-10-95-2010, 2010.

Kumai, M.: Snow crystals and the identification of the nuclei in the northern United States of America, J. Meteor., 18, 139-150, 1961.

Kumai, M.: Identification of nuclei and concentrations of chemical species in snow crystals sampled at South Pole, J. Atmos. Sci., 33, 833-841, 1976.

Ladino, L., Stetzer, O., Lüönd, F., Welti, A., and Lohmann, U.: Contact freezing experiments of kaolinite particles with cloud droplets, J. Geophys. Res., 116, D22202, doi:10.1029/2011JD015727, 2011.

Lelieveld, J., Berresheim, H., Borrmann, S., Crutzen, P. J., Dentener, F. J., Fischer, H., Feichter, J., Flatau, P. J., Heland, J., and Holzinger, R.: colleagues: Global air pollution crossroads over the Mediterranean. Science, 298, 794-799, 2002

Levi, Y. and Rosenfeld, D.: Ice nuclei, rainwater chemical composition, and static cloud seeding effects in Israel, J. Appl. Meteorol., 35, 1494-1501, 1996.

Levin, Z. and Lindberg, J. D.: Size distribution, chemical composition, and optical properties of urban and desert aerosol in Israel, J. Geophys. Res., 84, 6941-6950, 1979.

Levin, Z. and Yankofsky, S. A.: Contact versus immersion freezing of freely suspended droplets by bacterial ice nuclei, J. Clim. Appl. Meteorol., 22, 1964-1966, 1983.

Levin, Z., Joseph, J. H., and Mekler, Y.: Properties of Sharav (Khamsin) dust - comparison of optical and direct sampling data, J. Atmos. Sci., 37, 882-891, 1980.

Levin, Z. Yankofsky, S. A. Pardess D., and Magal, N.: Possible Application of bacterial condensation freezing to artificial rainfall enhancement, J. Climate and Appl. Meteor., 26, 1188-1197, 1987.

Levin Z., Price C., and Ganor, E.: The contribution of sulfate and desert aerosol to the acidification of cloud and rain in Israel, Atmos. Envir., 24, 1143-1151, 1990.

Levin, Z., Ganor, E., and Gladstein, V.: The effects of desert particles coated with sulfate on rain formation in the eastern Mediterranean, J. Appl. Meteor., 35, 1511-1523, 1996.

Levin, Z., Teller, A., Ganor, E., and Yin, Y.: On the interactions of mineral dust, sea salt particles and clouds - A Measurement and modeling study from the MEIDEX campaign, J. Geophys. Res., 110, D20202, doi:10.1029/2005JD005810, 2005.

Lohmann, U. and Diehl, K.: Sensitivity Studies of the Importance of Dust Ice Nuclei for the Indirect Aerosol Effect on Stratiform Mixed-Phase Clouds, J. Atmos. Sci., 63, 968-982, 2006.

Lüönd, F., Stetzer, O., Welti, A., and Lohmann, U.: Experimental study on the ice nucleation ability of size-selected kaolinite particles in the immersion mode, J. Geophys. Res., 115, D14201, doi:10.1029/2009JD012959, 2010.

Maki, L. R. and Willoughby, K. J.: Bacteria as biogenic sources of freezing nuclei, J. appl. Meteorol., 17, 1049-1053, 1978.

Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, Atmos. Chem. Phys., 7, 5081-5091, doi:10.5194/acp-7-5081-2007, 2007.

Meyers, M. P., DeMott, P. J., and Cotton, W. R.: New primary ice nucleation parameterizations in an explicit cloud model, J. Appl. Meteor., 31, 708-721, 1992.

Möhler, O., Field, P. R., Connolly, P., Benz, S., Saathoff, H., Schnaiter, M., Wagner, R., Cotton, R., Krämer, M., Mangold, A., and Heymsfield, A. J.: Efficiency of the deposition mode ice nucleation on mineral dust particles, Atmos. Chem. Phys., 6, 3007-3021, doi:10.5194/acp-6-3007-2006, 2006.

Murray, B. J., Broadley, S. L., Wilson, T. W., Atkinson, J. D., and Wills, R. H.: Heterogeneous freezing of water droplets containing kaolinite particles, Atmos. Chem. Phys., 11, 4191-4207, doi:10.5194/acp-11-4191-2011, 2011.

Murray, B. J., O'Sullivan, D., Atkinson, J. D., and Webb, M. E.: Ice nucleation by particles immersed in supercooled cloud droplets, Chem Soc Rev., 41, 6519-6554, doi: 10.1039/c2cs35200a, 2012.

Niedermeier, D., Hartmann, S., Shaw, R. A., Covert, D., Mentel, T. F., Schneider, J., Poulain, L., Reitz, P., Spindler, C., Clauss, T., Kiselev, A., Hallbauer, E., Wex, H., Mildenberger, K., and Stratmann, F.: Heterogeneous freezing of droplets with immersed mineral dust particles - measurements and parameterization, Atmos. Chem. Phys., 10, 3601-3614, doi:10.5194/acp-10-3601-2010, 2010.

Niedermeier, D., Shaw, R. A., Hartmann, S., Wex, H., Clauss, T., Voigtländer, J., and Stratmann, F.: Heterogeneous ice nucleation: exploring the transition from stochastic to singular freezing behavior, Atmos. Chem. Phys., 11, 8767-8775, doi:10.5194/acp-11-8767-2011, 2011.

Petters, M. D., Parsons, M. T., Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Carrico, C. M., Sullivan, A. P., McMeeking, G. R., Levin, E., Wold, C. E., Collett, J. L., and Moosmuller, H.: Ice nuclei emissions from biomass burning, J. Geophys. Res., 114, D07209, doi:10.1029/2008JD011532, 2009.

Philips, V. T. J., DeMott, P. J., and Andronache, C.: An empirical parameterization of heterogeneous ice nucleation for multiple chemical species of aerosol, J. Atmos. Sci., 65, 2757-2783, 2008.

Pinti, V., Marcolli, C., Zobrist, B., Hoyle, C. R., and Peter, T.: Ice nucleation efficiency of clay minerals in the immersion mode, Atmos. Chem. Phys., 12, 5859-5878, doi:10.5194/acp-12-5859-2012, 2012.

Pitter, R. L. and Pruppacher, H. R.: A wind tunnel investigation of freezing of small water drops falling at terminal velocity in air, Quart. J. Roy. Meteor. Soc., 99, 540-550, 1973.

Pratt, K. A., Murphy, S. M., Subramanian, R., DeMott, P. J., Kok, G. L., Campos, T., Rogers, D. C., Prenni, A. J., Heymsfield, A. J., Seinfeld, J. H., and Prather, K. A.: Flight-based chemical characterization of biomass burning aerosols within two prescribed burn smoke plumes, Atmos. Chem. Phys., 11, 12549-12565, doi:10.5194/acp-11-12549-2011, 2011.

Prenni, A. J., Demott, P. J., Rogers, D. C., Kreidenweis, S. M., Mcfarquhar, G. M., Zhang, G., and Poellot, M. R.: Ice nuclei characteristics from M-PACE and their relation to ice formation in clouds, Tellus, 61, 436-448, 2009a.

Prenni, A. J., Petters, M. D., Kreidenweis, S. M., Heald, C. L., Martin, S. T., Artaxo, P., Garland, R. M., Wollny A. G., and Pöschl, U.: Relative roles of biogenic emissions and Saharan dust as ice nuclei in the Amazon basin, Nat. Geosci., 2, 402-405, 2009b.

Prenni, A. J., DeMott, P. J., Sullivan, A. P., Sullivan, R. C., Kreidenweis, S. M., and Rogers, D. C.: Biomass burning as a potential source for atmospheric ice nuclei: Western wildfires and prescribed burns, Geophys. Res. Lett., 39, L11805, doi:10.1029/2012GL051915, 2012.

Pruppacher, H. R. and Klett, J. D.: Microphysics of Clouds and Precipitation, Kluwer, Norwell, 1997.

Roberts, P. and Hallett, J: A laboratory study of the ice nucleating properties of some mineral particulates, Quart. J. Roy. Meteor. Soc., 94, 25-34, 1968.

Santachiara, G., Di Matteo, L., Prodi, F., and Belosi, F.: Atmospheric particles acting as Ice Forming Nuclei in different size ranges, Atmos. Res., 96, 266-272, 2010.

Salam, A., Lohmann, U., and Lesins, G.: Ice nucleation of ammonia gas exposed montmorillonite mineral dust particles, Atmos. Chem. Phys., 7, 3923-3931, doi:10.5194/acp-7-3923-2007, 2007.

Sarnat, J. A., Moise, T., Shpund, J., Yang, L., Pachon, J. E., Qasrawi, R., Abdeen, Z., Brenner, S., Nassar, K., Saleh, R., and Schauer, J. J.: Assessing the spatial and temporal variability of fine particulate matter components in Israeli, Jordanian, and Palestinian cities, Atmos. Environ., 44, 2383–2392 2010.

Schnell, R. and Vali, G: Biogenic Ice Nuclei: Part I. Terrestrial and Marine Sources, J. Atmos. Sci., 33, 1554-1564, 1976.

Schnell, R. C., Pueschel, R. F., and Wellman D. L.: Ice nucleus characteristics of Mount St. Helens effluents, J. Geophys. Res., 87, 11109-11112, 1982.

Seifert, M., Ström, J., Krejci, R., Minikin, A., Petzold, A., Gayet, J. F., Schumann, U., and Ovarlez, J.: In-situ observations of aerosol particles remaining from evaporated cirrus crystals: Comparing clean and polluted air masses, Atmos. Chem. Phys., 3, 1037-1049, doi:10.5194/acp-3-1037-2003, 2003.

Seifert, P., Ansmann, A., Mattis, I., Wandinger, U., Tesche, M., Engelmann, R., Müller, D., Perez, C., and Haustein, K.: Saharan dust and heterogeneous ice formation: Eleven years of cloud observations at a central European EARLINET site, J. Geophys. Res., 115, D20201, doi:10.1029/2009JD013222, 2010.

Twohy, C. H. and Poellot, M. R.: Chemical characteristics of ice residual nuclei in anvil cirrus clouds: evidence for homogeneous and heterogeneous ice formation, Atmos. Chem. Phys., 5, 2289-2297, doi:10.5194/acp-5-2289-2005, 2005.

Vali, G.: Filetr-elutriition experiments for the measurement of airborne freezing nuclei, J. de. Rech. Atmos., 3(2), 175-177, 1968.

Vali, G.: Quantitative evaluation of experimental results on the heterogeneous freezing nucleation of supercooled liquids, J Atmos. Sci., 28, 402-409, 1971.

Vali, G.: Repeatability and randomness in heterogeneous freezing nucleation, Atmos. Chem. Phys., 8, 5017-5031, doi:10.5194/acp-8-5017-2008, 2008.

Van den Heever, S.C., Carrio, G.G. Cotton, W.R. DeMott, P.J., and Prenni, A.J.: Impacts of nucleating aerosol on Florida convection. Part I: Mesoscale Simulations, J. Atmos. Sci., 63, 1752-1775, 2006.

von Schneidemesser, E., Zhou, J., Stone, E. A., Schauer, J. J., Shpund, K., Brenner, S., Barakat, R., Abdeen, Z., and Sarnat, J. A.: Spatial Variability of Carbonaceous Aerosol Concentrations in East and West Jerusalem. Environ. Sci. Technol., 44 (6), 1911-1917, 2010.

Welti, A., Lüönd, F., Stetzer, O., and Lohmann, U.: Influence of particle size on the ice nucleating ability of mineral dusts, Atmos. Chem. Phys., 9, 6705-6715, doi:10.5194/acp-9-6705-2009, 2009.

Welti, A., Lüönd, F., Kanji, Z. A., Stetzer, O., and Lohmann, U.: Time dependence of immersion freezing: an experimental study on size selected kaolinite particles, Atmos. Chem. Phys., 12, 9893-9907, doi:10.5194/acp-12-9893-2012, 2012.

Zhang, D., Wang, Z., Heymseld, A., Fan, J., Liu, D., and Zhao, M.: Quantifying the impact of dust on heterogeneous ice generation in midlevel supercooled stratiform clouds, Geophys. Res. Lett., 39, L18805, doi:10.1029/2012GL052831, 2012.

Zimmermann, F., Weinbruch, S., Schütz, L., Hofmann, H., Ebert, M., Kandler, K., and Worringen, A.: Ice nucleation properties of the most abundant mineral dust phases, J. Geophys. Res., 113, D23204, doi:10.1029/2008JD010655, 2008.

Table 1: List of filters sampled, total concentrations of particles and PM values.

# Filter	Date	CPC_{3010} number concentration ($\#/cm^3$)	PM_{10} day average ($\mu g\ m^{-3}$)	$PM_{2.5}$ day average ($\mu g\ m^{-3}$)	Classification
1	24 Jan 2009	639.7±34.8	841.7±619.7	212.3±152.8	Dust storm
2	15 Feb 2009	726.8±100.6	245.4±126.9	44.4±21.9	Dust storm
3	19 Feb 2009	1251.2±66.7	441.9±506	100.1±93.8	Dust storm
4	08 Mar 2009	515.6±26.9	317.8±173.7	76.5±37.7	Not classified
5	15 Mar 2009	1964.3±225.7	39±12.6	12.6±4.9	Clean
6	16 Jun 2009	1158.6±24.1	35.4±10.9	19.7±7	Clean
7	21 Sep 2009	841±80.5	29.9±8.9	22.3±11.1	Clean
8	22 Oct 2009	422.9±42.5	31.3±12.2	21.2±11.6	Clean
9	1 Nov 2009	1865.4±101.3	84.4±42.2	21.4±8.9	Not classified
10	17 Dec 2009	1825.7±328.6	677.6±494.4	153.8±105.4	Dust storm
11	30 Jan 2010	718.4±153	383.4±426.1	59.7±53.1	Dust storm
12	09 Mar 2010	1600.2±66.1	408.1±229.4	83.5±43.9	Dust storm
13	11 Apr 2010	436.7±54.5	351.6±469	72.5±77.9	Dust storm
14	01 May 2010_15*	563.9±15.2	36.4±9	21.2±7	Clean
15	01 May 2010_23*	1344.8±97.2	36.4±9	21.2±7	Lag Ba Omer
16	27 May 2010	751.9±46.3	867.2±745.2	154.6±130.8	Dust storm
17	15 Nov 2010	2626.3±54.1	93.5±21.3	44.6±18.6	Not classified
18	30 Dec 2010	1552.1±171.7	88.7±21.3	29.7±8.5	Not classified
19	31 Dec 2010	612.2±31.3	49.2±27.7	21±11.2	Not classified

* Two samples were collected on the same day (01 May 2010) at 15:00 and at 23:00 local time (during Lag BaOmer celebration).

Table 2: Results of the onset of freezing temperature, median temperature and the temperature of the last freezing drop in each sample. List of the freezing spectra of all measured filters and the average spectrum of freezing temperature from clean (blank) filters and blank (pure) water.

Filter	Date	Onset of freezing temperature (°C)	Median freezing temperature(°C)	Freezing temperature of the last drop in each sample (°C)
1	24 Jan 2009	-15.6	-20.1	-24.1
2	15 Feb 2009	-12.8	-21.1	-25.5
3	19 Feb 2009	-16	-19.9	-22.6
4	08 Mar 2009	-15.8	-21.7	-26.8
5	15 Mar 2009	-15.3	-20.5	-21.4
6	16 Jun 2009	-19.7	-24.4	-28.9
7	21 Sep 2009	-18.9	-22.1	-25.6
8	22 Oct 2009	-15.9	-20.3	-26.3
9	1 Nov 2009	-15	-21.2	-25.3
10	17 Dec 2009	-12.8	-17.8	-21.5
11	30 Jan 2010	-15.5	-20.8	-23.1
12	09 Mar 2010	-14.8	-19.7	-24.2
13	11 Apr 2010	-16.9	-21.7	-24
14	01 May 2010_15	-15.5	-22.2	-26.1
15	01 May 2010_23	-17.9	-21.7	-26.6
16	27 May 2010	-11.8	-19.3	-23.8
17	15 Nov 2010	-16	-21.4	-24.8
18	30 Dec 2010	-17.7	-22	-25.6
19	31 Dec 2010	-17.8	-21.6	-26.7
	Blank (clean) water	-23	-32.3	-40
	Blank filter	-26	-35.6	-40

Table 3: Summary of clean and dust storms conditions

Date	Dust storms days	Clean days
Number of days	8	5
Average PM_{10} values (µg m^{-3})	527±236	34±3.8
Average $PM_{2.5}$ values (µg m^{-3})	110±58	19±3.6
Average $PM_{10-2.5}$ values (µg m^{-3})	417±182	15±7.2
Number of droplets used	1173	626
Temperature at which the first drops froze (°C)	-11.8	-15.3
Median temperature of frozen drops (°C)	-20±1.2	-21.9±1.5
Temperature at which the last drop froze (°C)	-25.1	-27.4

Table 4: Frequency of occurrence (%) of elemental composition of 203 individual particles from two samples collected on May 27 and Nov 15, 2010, as measured by individual particle analysis using an ESEM and EDS.

Elements	Frequency of occurrence (%)
Calcium (Ca)	93.1
Silicon (Si)	67.5
Aluminum (Al)	59.6
Iron (Fe)	50.7
Magnesium (Mg)	45.3
Potassium (K)	31.5
Chlorine (Cl)	16.3
Sulfur (S)	7.4
Titanium (Ti)	3.9
Sodium (Na)	3.4
Bromine (Br)	3.4
Barium (Ba)	1.0
Molybdenum (Mo)	1.0
Zinc (Zn)	0.5
Copper (Cu)	0.5
Manganese (Mn)	0.5

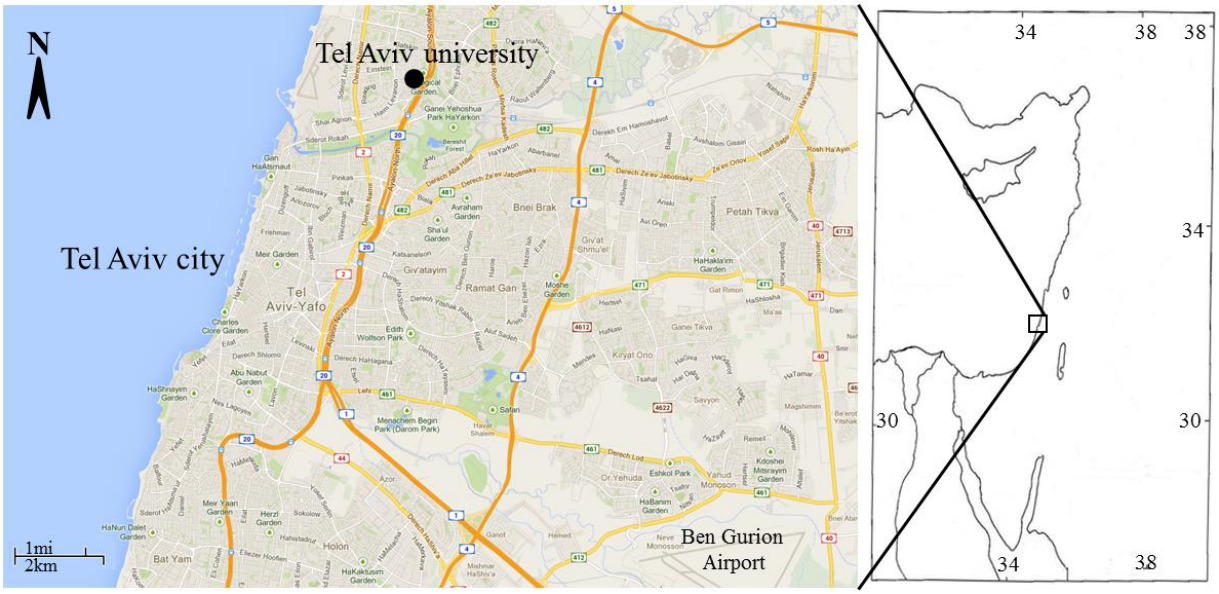

Fig. 1: Location of the sampling station at Tel Aviv University marked in black (Google map, with modification, 2012).

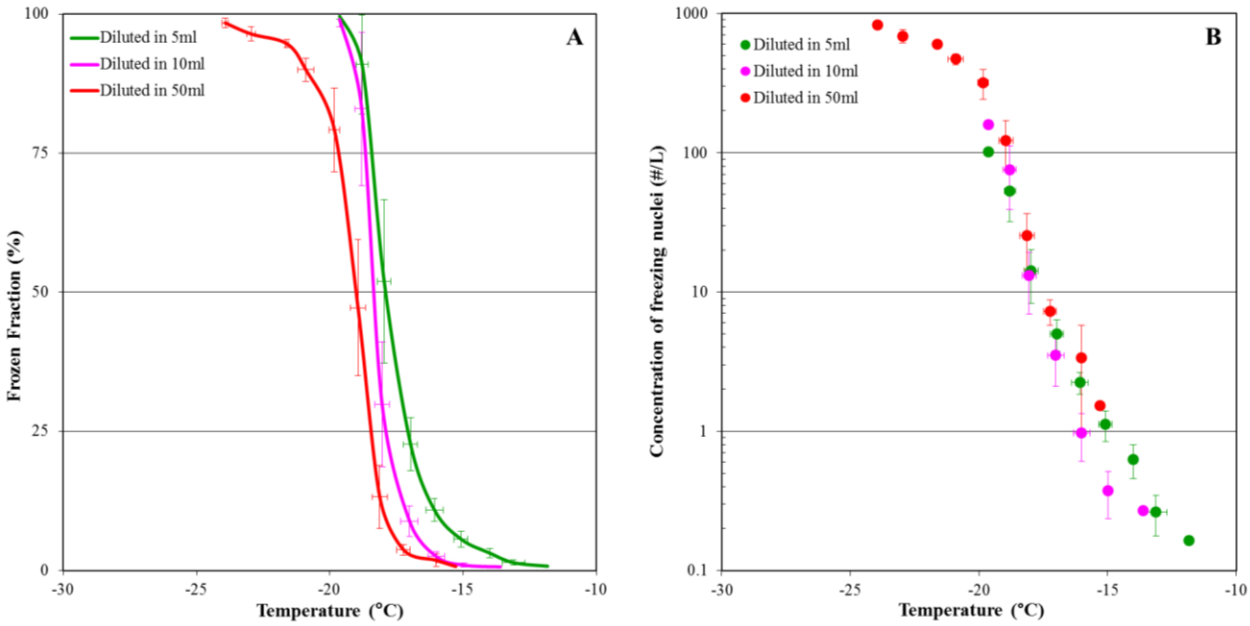

Fig. 2: Results of freezing experiments using montmorillonite particles: (A) Cumulative frozen fraction as a function of temperature of all three dilution experiments. (B) FN concentration calculated as a function of temperature for the different dilution experiments.

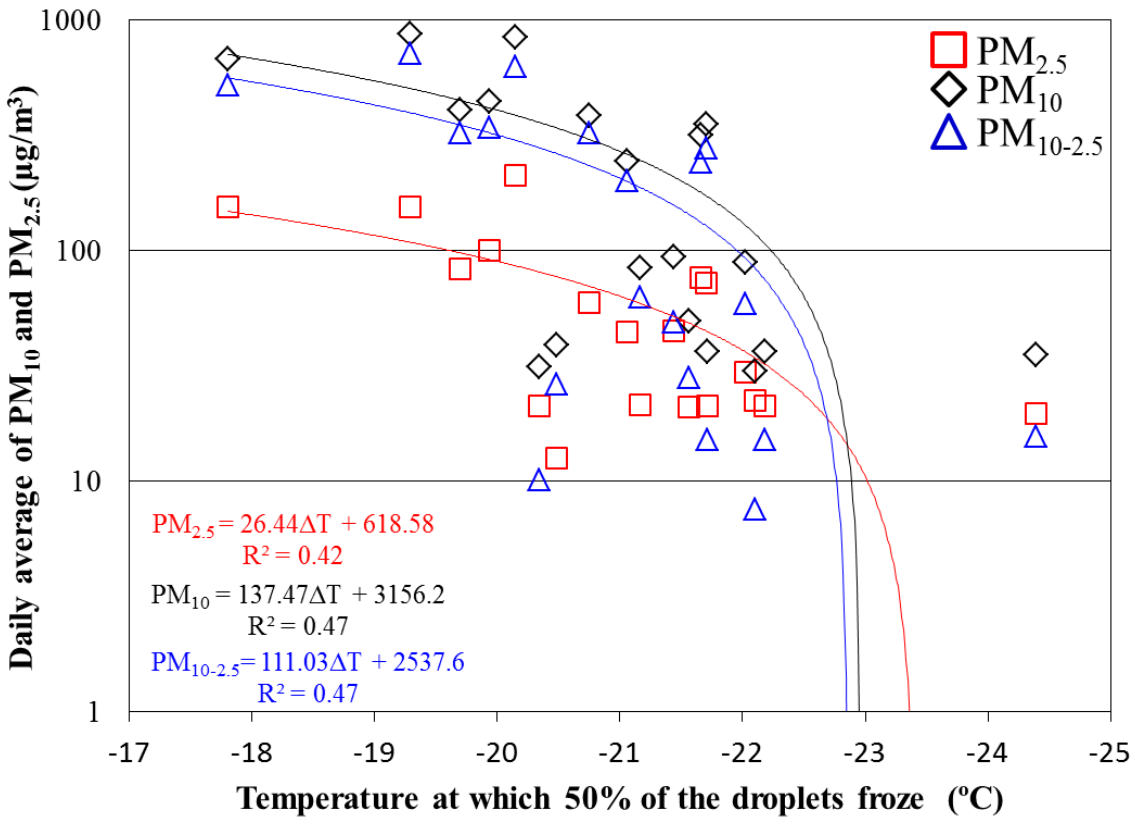

Fig. 3: The connection between the median freezing temperature of the drops and the daily average values of $PM_{2.5}$ (in red), PM_{10} (in black), and PM_{10}-$PM_{2.5}$ (in blue).

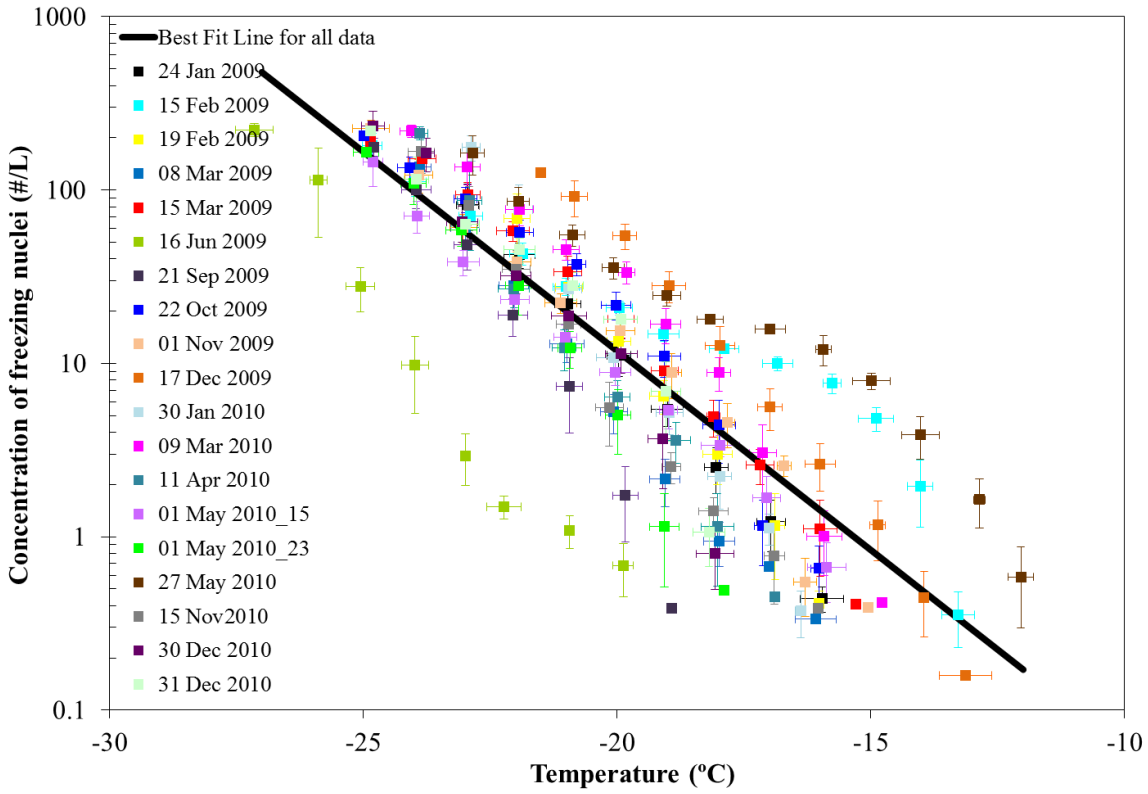

Fig. 4: The concentrations of FN using the different filters. The bars represent the standard deviation and the black line is the best-fit line representing all the data. Please note the significantly low values of the measurements during the Lag BaOmer bonfires at 23:00 (green squares).

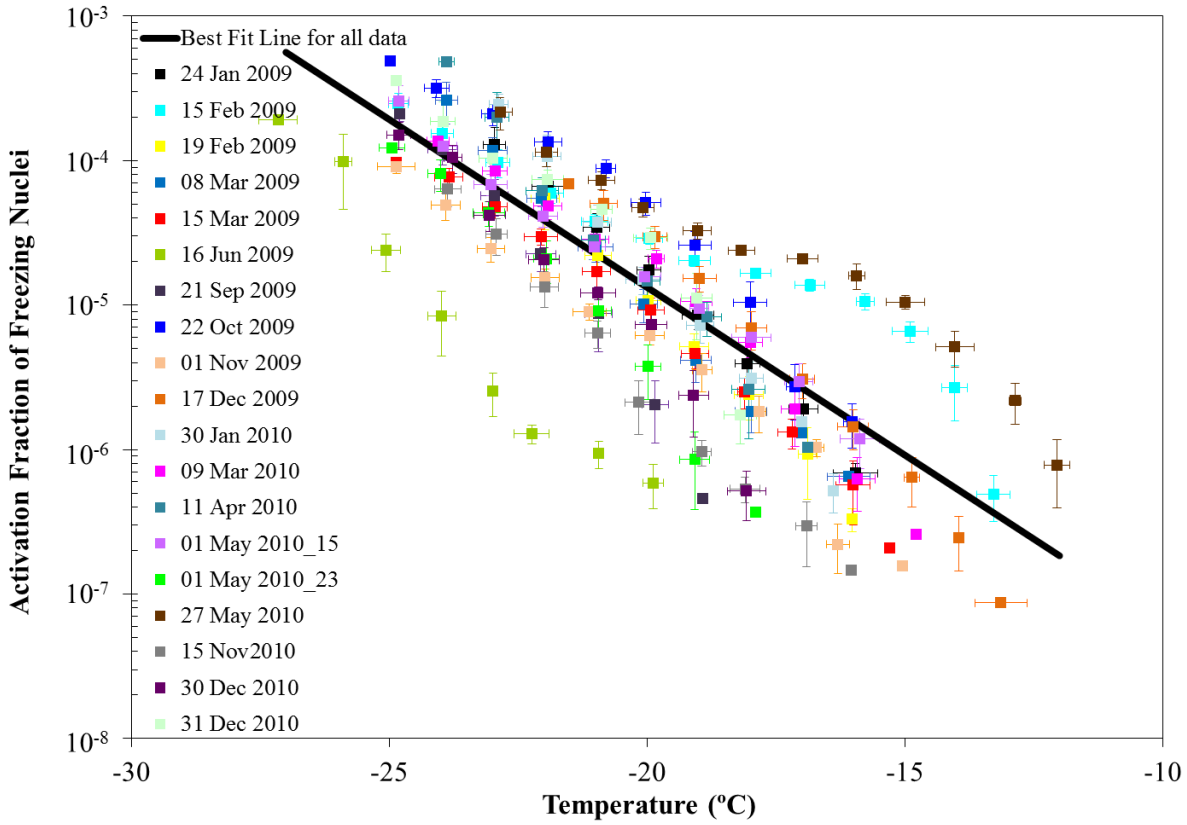

Fig. 5: Activated fraction of FN calculated with standard deviation values for the different filters. Each color represents a different sample while the black line is the best-fit line.

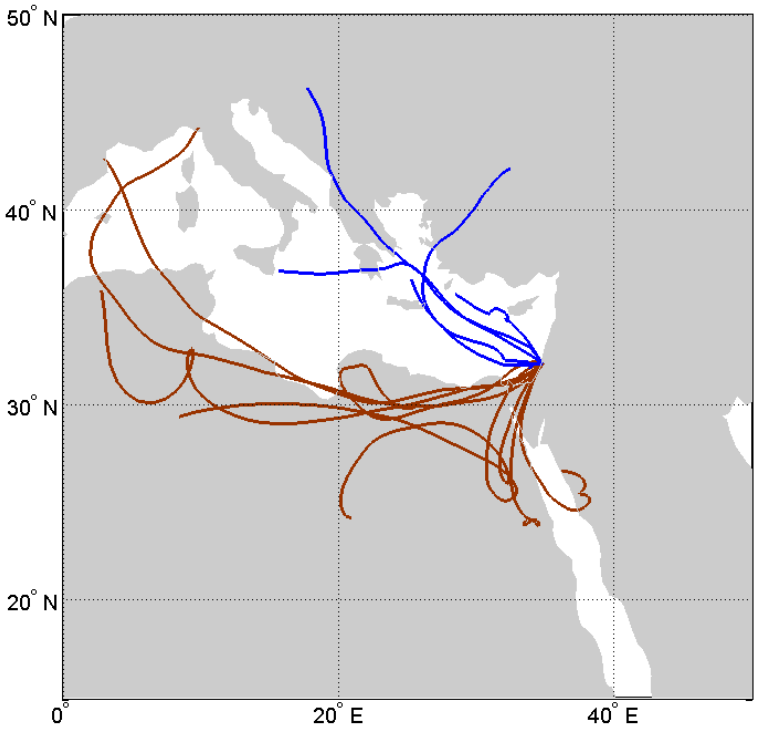

Fig. 6: Back trajectory history of air masses showing passage of air prior to reaching the sampling station. Each line represents a 72 hour trajectory at 500m altitude. The back trajectories were taken from http://www.arl.noaa.gov website. The brown lines represent dust storm conditions and the blue lines represent clean conditions.

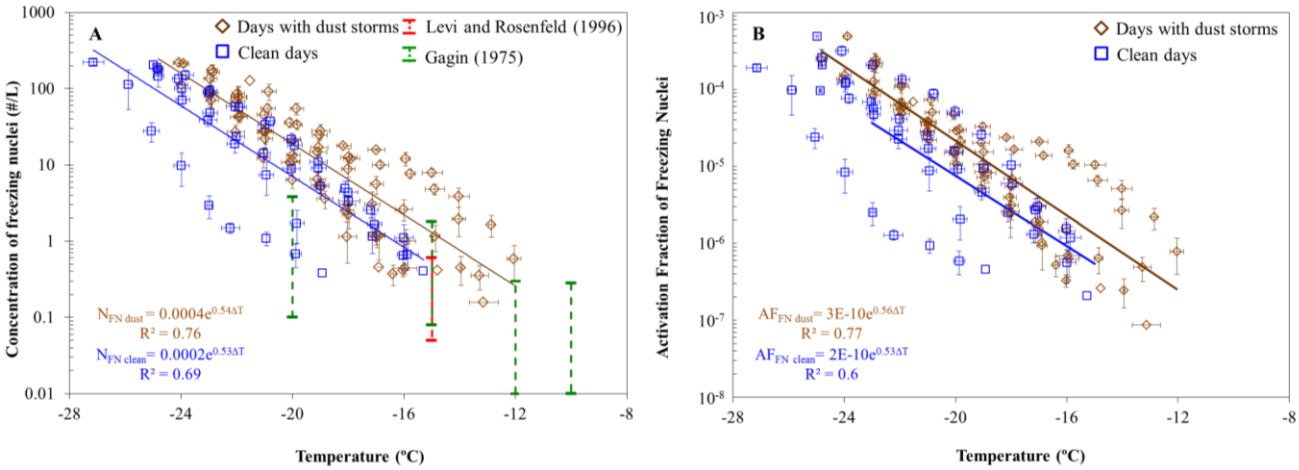

Fig. 7: Freezing nuclei concentration (A) and activated fraction values (B) with standard deviation, calculated for clean (blue) and dust storm (brown) days. Best-fit lines and the equations that represent them are also shown. For comparison in (A) the ice nuclei concentrations measured in Israel near cloud base by Gagin (1975) (green bars) and ground measurements by Levi and Rosenfeld (1996) (red bars) are also shown.

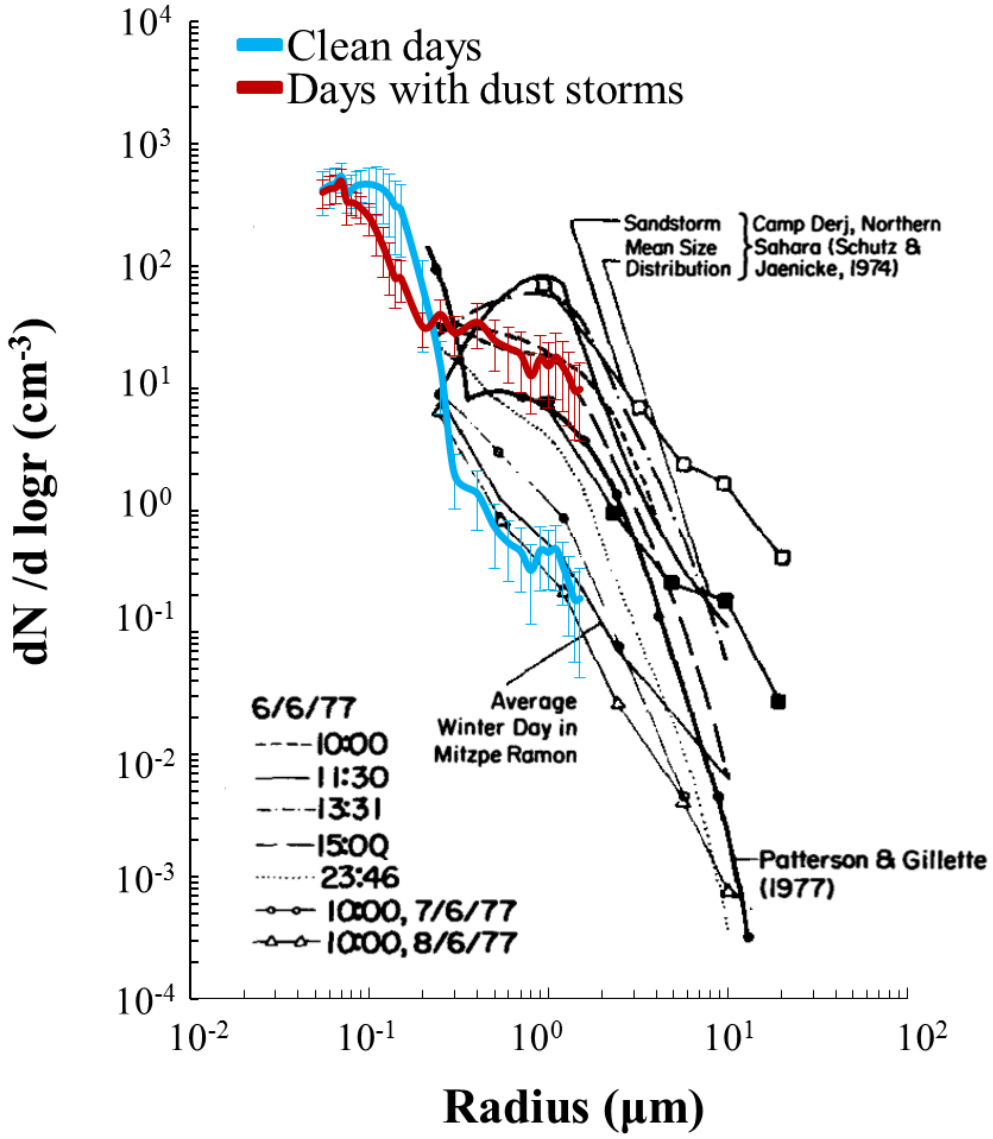

Fig. 8: Average size distributions and standard deviation as measured during dust storm and clean days (in brown and blue, respectively) plotted on top of the results of dust particle measurements in Israel and in other locations as presented by Levin et al. (1980).

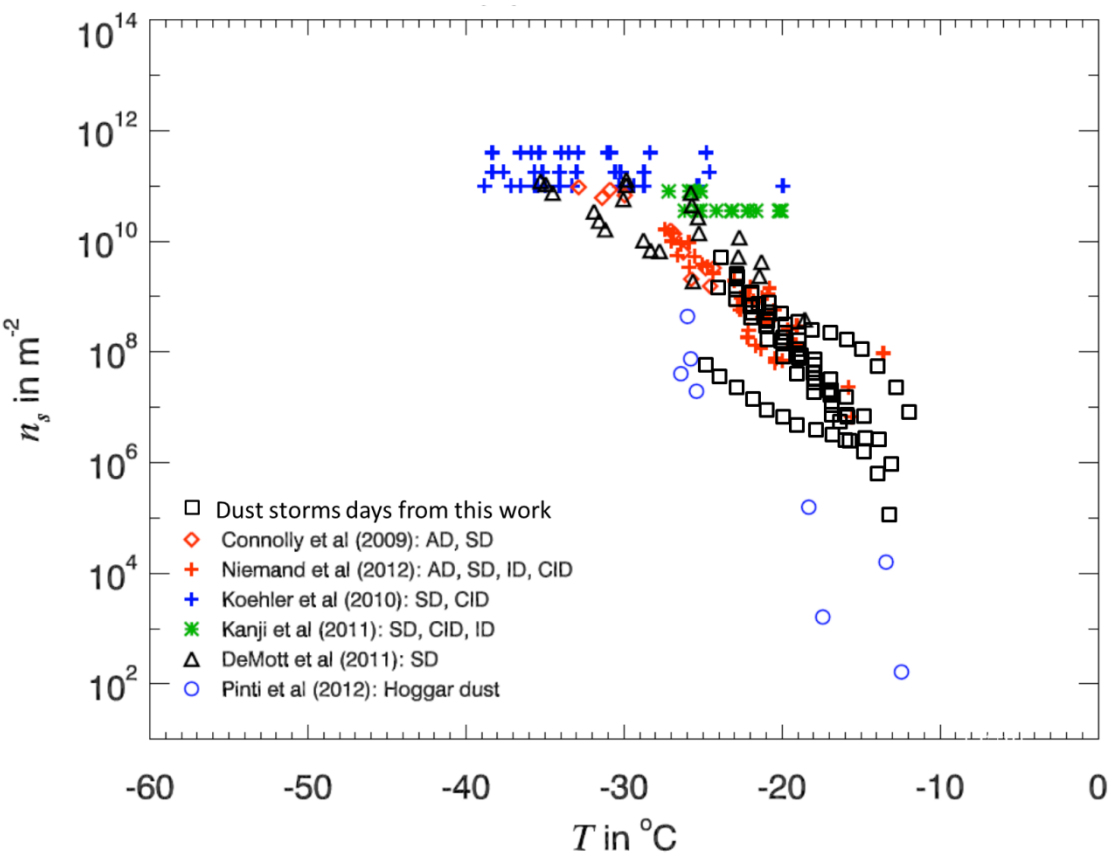

Fig. 9. INAS densities as a function of temperature from Hoose and Möhler (2012) with dust storm days from this work in black squares. It is worth noting the similarity between the present results from immersion freezing and those obtained by different nucleation mode and using different types of desert dusts such as Asian dust (AD), Canary Island dust (CID), Saharan dust (SD) and Israeli dust (ID).

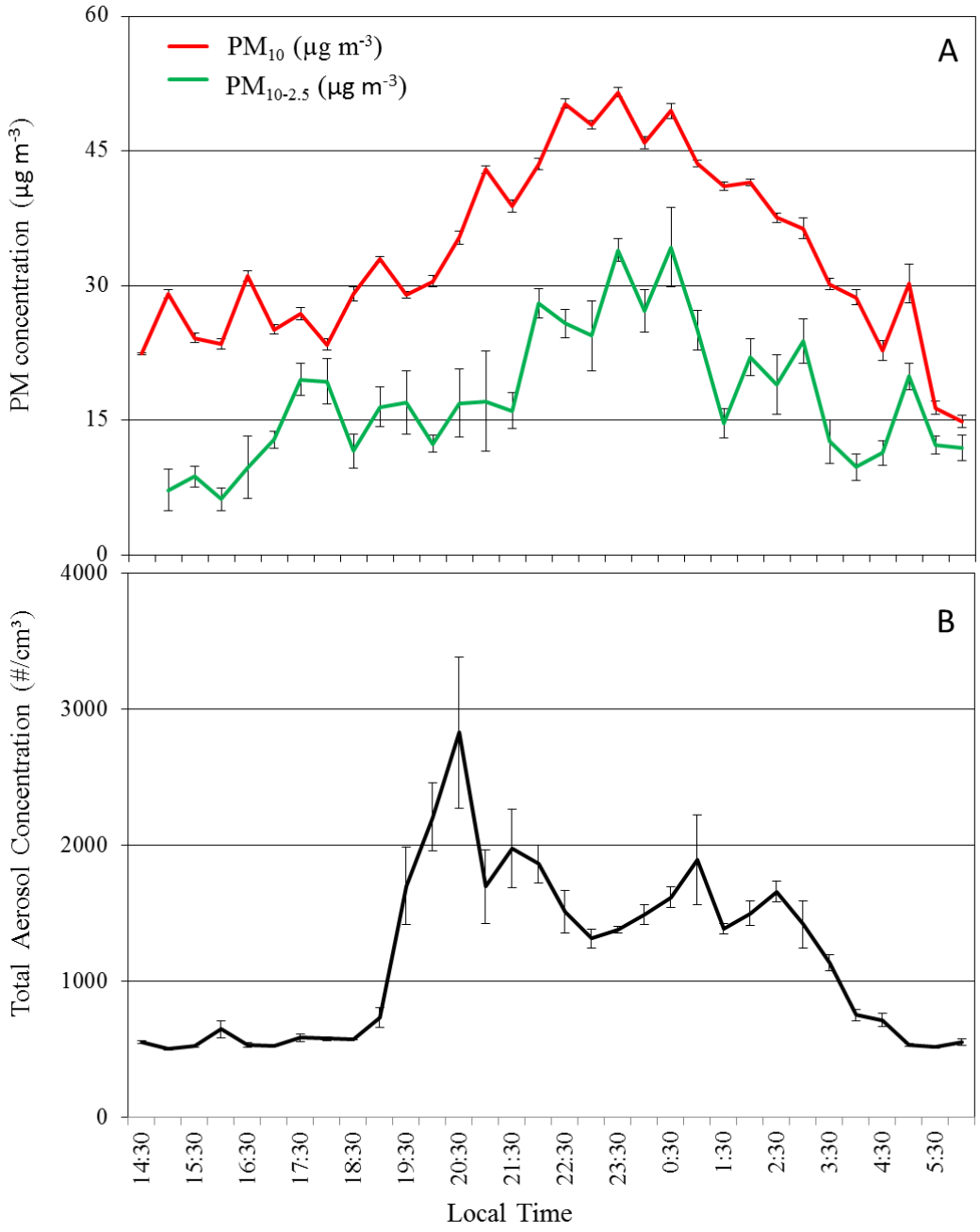

Fig. 10: PM_{10} (in red) and $PM_{10\text{-}2.5}$ concentration (in green) and aerosol total concentration (in black), as measured during May 01 – 02, 2010. The data are averaged over 30 min and the bars represent the standard deviation. The bonfires started around 19:00 and ended around 03:00 the next morning as rain began to fall.