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Atmospheric Measurement Techniques

Atmospheric ice nucleators active $\geq -12\,^{\circ}\mathrm{C}$ can be quantified on PM_{10} filters

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Abstract. Small number concentrations render it difficult to quantify ice nucleators (IN) in the atmosphere active at warm temperatures. A useful new method for IN measurement based around filter collections is proposed. It makes use of quartz filters used in 24 h PM_{10} monitoring (720 m^3 air sample). Small subsamples (1.8 mm diameter) from the effective filter area and from the clean fringe (blank) are subjected to immersion freezing tests. We applied the method to eight filters from the High Alpine Research Station Jungfraujoch (3580 m above sea level) in the Swiss Alps. All filters carried IN active at $-7\,^{\circ}\mathrm{C}$ and below. Number concentrations of IN active at -8, -10, and $-12\,^{\circ}\mathrm{C}$ were on average 3.3, 10.7, and 17.2 m^{-3}, respectively. Several-fold larger numbers of IN active at $\geq -12\,^{\circ}\mathrm{C}$ per unit mass of PM_{10} were found in air masses influenced by Swiss and southern German atmospheric boundary layer air, compared to a Saharan dust event. In combination with data on PM_{10} mass, the method may be used to re-construct time series of IN number concentrations.

1 Motivation

Precipitation release from stratiform clouds in mid- and high latitude is largely influenced by the formation of ice crystals (Phillips et al., 2003) and their growth at the expense of liquid cloud droplets, as described by the Wegener-Bergeron-Findeisen process. Homogeneous freezing of micrometre-sized water aerosol droplets occurs at approximately -36 to $-37\,^{\circ}\mathrm{C}$ (Murray et al., 2010). A range of natural and anthropogenic particles in the atmosphere is capable of initiating freezing at much warmer temperatures, a process called heterogeneous freezing nucleation. It can been assumed that all naturally occurring ice nucleators (IN) active at temperatures warmer than $-10\,^{\circ}\mathrm{C}$ are of biological origin (Christner et al., 2008). Although numerical simulations suggest a negligible role of biological IN on the global scale (Hoose et al., 2010a, b), a quarter of clouds observed over Central Europe with cloud top temperatures of $-10\,^{\circ}\mathrm{C}$ contained measurable amounts of ice (Seifert et al., 2010), so are probably influenced by biological IN.

To assess the influence of biological IN on climate, long-term observations in different regions are essential. However, the small number concentration of biological IN renders meaningful time-resolved measurements with continuously operating flow-through IN counters impractical (Möhler et al., 2007). Here, pre-concentration and off-line counting techniques are beneficial. Collection of IN on a membrane filter (e.g. "Millipore"), subsequent exposure of the filter to cold and moist conditions, and counting of the ice crystals that grow, is a method that was developed 50 yr ago by Bigg et al. (1961). It was improved by Stevenson (1968) and later by Langer and Rodgers (1975). Although it is still in use today, the method was more widely applied during the 1970s (e.g. Bigg, 1973; Hobbs and Atkinson, 1976; Schnell and Delany, 1976; Bowdle et al., 1985; Rosinski and Morgan, 1991; Santachiara et al., 2010).

Today, particulate matter $\leq 10\,\mu\mathrm{m}$ (PM_{10}) is routinely collected in many places for monitoring the atmospheric concentration of this public health hazard. Instead of membrane filters, quartz fibre filters are generally used in this application. Often, only part of the sampled material is consumed

in further analysis. If the remainder could be analysed for IN number concentrations, it would offer a convenient way to obtain number concentrations of IN without additional investment into a sampling infrastructure. Particular questions could be studied by retrospectively selecting suitable filters from existing archives. However, PM_{10} filters can not be analysed for IN in the same way as membrane filters, because particles are embedded in the felt-like, three-dimensional structure of the quartz fibre filter material ($\sim$0.5 mm thick).

2 Approach, materials and methods

2.1 Site and sampling

The Swiss National Air Pollution Monitoring Network (NABEL) operates a high volume sampler (model DA-80 H, Digitel Elektronik AG, 8604 Hegnau, Switzerland) at the High Alpine Research Station Jungfraujoch (JFJ, 7°59′2″ E, 46 °32′53″ N, 3580 m a.s.l.). Apart from the high volume sampler for PM_{10}, NABEL's current measurement program at JFJ also includes continuous PM_{10} observations and in-situ analyses of ozone, carbon monoxide, nitrogen oxides, sulfur dioxide and a comprehensive set of greenhouse gases and ozone-depleting substances. Meteorological parameters are measured by the Swiss Federal Office of Meteorology and Climatology MeteoSwiss. JFJ is mostly situated in the free troposphere and considered a remote measurement site. However, it intermittently receives air masses influenced by the European atmospheric boundary layer, brought up to the site by either frontal passages, foehn situations or thermally-induced flow systems (Zellweger et al., 2003; Henne et al., 2010).

PM_{10} is collected from the atmosphere daily for 24 h on quartz fiber filters (Pallflex Tissuquartz, Pall Corporation, Port Washington, NY 11050, USA) at an air flow rate of $30\,m^3\,h^{-1}$. After analysis, 1/2 to 3/4 of the filter area is left over. Filter diameter is 150 mm, with an effective diameter of 140 mm. A 5 mm wide fringe, where the filter is covered by sampler parts, is not exposed to the passing air stream. We selected eight filters collected between 10 June and 11 July 2010 which had sampled air masses of different geographical origin. Conen et al. (2011) suggested that larger numbers of IN per unit mass of soil dust may be found in colder, compared to warmer regions. Our filter selection served to test whether – in principle – such differences may be detectable through the analysis of PM_{10} filters.

2.2 Filter analysis

Initial attempts to quantitatively extract PM_{10} from the felt-like filter material were not successful, because no matter what procedure we applied, there was no way to quantitatively extract all particles without extracting at the same time much larger amounts of quartz fibers. When subsequent tests indicated that clean quartz filter material did not carry significant numbers of IN active within our temperature range of interest ($\geq -12\,^{\circ}C$), we decided to leave the particles on the filter material and subject the ensemble to immersion freezing tests. From the effective sampling area of each filter, 108 small circles of 1.8 mm diameter were cut out with the sharpened end of a stainless steel tube bit. For control, another 108 circles were taken from the 5 mm clean fringe of the same filter. Freezing tests for sample and blank consisted of placing each 1.8 mm diameter circle in a separate 0.5 ml Eppendorf tube, adding 0.1 ml filtered (<0.2 µm) Milli-Q water and exposing it to decreasing temperatures ($0.33\,^{\circ}C\,min^{-1}$) in a cooling water bath. After each 1 °C step in temperature, the tubes were inspected visually and the number of frozen tubes was recorded. The cumulative number of ice nucleation sites active at the observation temperature or warmer in $1\,m^3$ air (K_T) was calculated similar to Vali (1971) as:

$$K_T = [\ln(N_{total}) - -\ln(N_{unfrozen})]/a \quad (1)$$

where N_{total} is the total number of tubes (108), $N_{unfrozen}$ is the number of tubes still unfrozen (liquid) at the observation temperature, and a is the volume of air that has passed through the 1.8 mm filter section ($a = 0.12\,m^3$). Although no air passed through the clean fringe area of the filter, we use the same value for a as for the sample area to get an equivalent number of IN m^{-3}. Dividing the number of IN m^{-3} by the mass of PM_{10} in $1\,m^{-3}$ provides the number of IN per unit mass of PM_{10}. Also two completely blank filters were tested.

2.3 Air mass origin

The origin of the sampled air masses was investigated using the Lagrangian Particle Dispersion Model (LPDM) FLEXPART (Stohl et al., 2005) in backwards mode. For each 24-h period covered by the individual filters 400 000 model particles were released at the location of JFJ and followed backward in time for 10 days. Simulations were driven by 3-hourly European Centre for Medium range Weather Forecast (ECMWF) operational model fields, alternating between analysis (00:00, 06:00, 12:00, 18:00 UTC) and forecast (03:00, 09:00, 15:00, 21:00 TUC) fields. The horizontal resolution of these fields was 1° by 1° for the global and 0.2° by 0.2° for a nested domain covering Central Europe. Owing to the altitude mismatch between model and real world topography, particles were not released at station height but at 3000 m a.s.l., which proved to yield most realistic results in previous studies (Keller et al., 2010; Brunner et al., 2011). For each filter sample, total source sensitivities (also called footprints) (Seibert and Frank, 2004) between the surface and 100 m above model ground were calculated.

Table 1. Data on PM_{10} filters analysed and number of ice nucleators detected (m^{-3}).

Sampling date	10 June	11 June	29 June	30 June	01 July	09 July	10 July	11 July
Source area	N-Italy		Switzerland/S-Germany			N-Africa/Switzerland		
Air temp. (°C)	−1	0	1	3	3	7	6	5
Rel. hum. (%)	98	96	92	71	78	42	72	74
Wind speed ($m\,s^{-1}$)	22	14	2	1	1	4	4	2
CO (ppbv)	123	127	136	128	137	94	110	109
PM_{10} ($\mu g\,m^{-3}$)	5.9	7.1	7.8	5.9	6.6	18.9	28.0	14.8
T (°C)	Number of IN m^{-3} air *Effective sampling area of filter*							
−4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
−5	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00
−6	0.00	0.08	0.00	0.00	0.00	0.00	0.08	0.00
−7	0.08	0.65	1.53	0.48	0.40	0.48	0.90	0.48
−8	0.73	4.94	5.67	3.29	2.73	2.01	3.18	3.89
−9	1.53	7.94	11.05	8.78	6.47	3.89	7.36	7.17
−10	2.01	11.65	15.53	13.76	14.60	6.30	9.47	11.96
−11	2.84	15.05	17.79	18.46	19.19	7.74	10.49	17.79
−12	3.89	16.59	27.69	21.87	24.28	9.00	12.64	21.87
	Clean fringe of filter (upper estimate of blank)							
−4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
−5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
−6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
−7	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00
−8	0.00	0.16	0.24	0.08	0.00	0.08	0.16	0.00
−9	0.00	0.16	0.40	0.08	0.32	0.08	0.24	0.48
−10	0.00	0.16	0.40	0.16	0.56	0.16	0.32	1.17
−11	0.00	0.24	0.40	0.24	0.65	0.24	0.65	1.35
−12	0.16	0.40	0.40	0.24	0.65	0.40	1.08	1.63

3 Results and discussion

3.1 Background counts

It is unlikely that the quartz fibres act as IN. Of the two completely blank filters right out of the suppliers pack, only 1 in 216 tubes, each containing a circle of 1.8 mm diameter of filter material, froze at $\geq -12\,^{\circ}C$ (at $-8\,^{\circ}C$), equivalent to an average of 0.04 IN m^{-3}. Clean fringes of the filters that had been used for PM_{10} sampling showed larger values (Table 1). At $-10\,^{\circ}C$ these values were equivalent to between 0.00 and 1.17, and on average 0.36 IN m^{-3}. Numbers of ice nucleation sites active at $-12\,^{\circ}C$ on the effective filter area (PM_{10} sample) were on average 39 times larger than on the clean fringe of the same filter. Probably, material from the dusty part of the filter had been transferred to the clean fringe during filter handling. Hence the clean fringe of the filters provide an upper estimate of the blank counts.

3.2 Number concentrations of IN

All samples had IN active at $-7\,^{\circ}C$. The warmest freezing temperature observed was at $-5\,^{\circ}C$ (Table 1). Numbers of IN active at $-10\,^{\circ}C$ were between 2.0 and 15.5 m^{-3} air. Interception of IN by the small areas that we later cut out of the filter for analysis is a stochastic process. Numbers of IN detected per m^3 are small. Each number was obtained from the analysis of 108 filter bits, each of which had collected aerosol particles from 0.12 m^3. Hence, a value of 10 IN m^{-3} is based on a total of 130 IN detected in 13 m^3 of air. The total number of IN detected has a standard deviation of 11.4 (square root of 130) and the number of IN m^{-3} has a standard deviation of 0.88 (11.4/13). Consequently, the 95 % confidence interval for a value of 10 IN m^{-3} ranges from 8.24 to 11.76.

Bowers et al. (2009) conducted measurements at a slightly lower altitude in the United States (Storm Peak Laboratory, 40°27′00″ N, 106°43′48″ W, 3200 m a.s.l.) with a membrane filter technique (0.22 µm). They washed particles from the membrane filters to subject them to drop freeze tests.

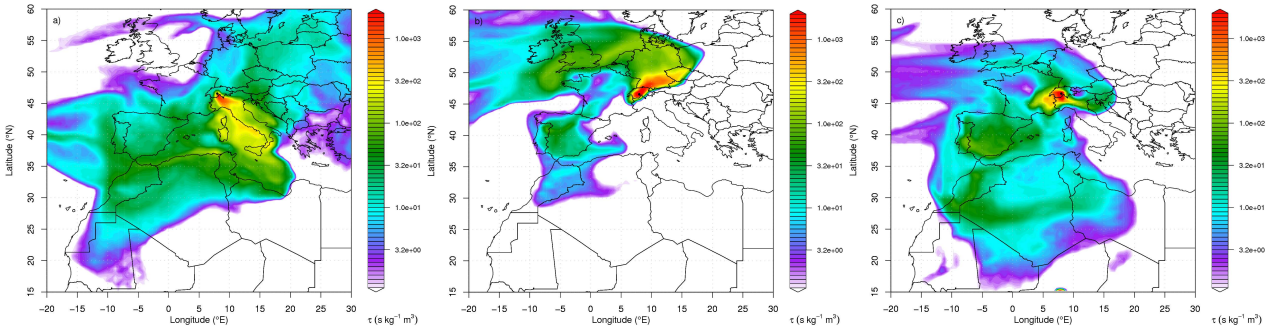

Fig. 1. Surface source sensitivities (footprints) for grouped filter samples: (left) 10–11 June 2010, North Italian influence, (centre) 29 June to 1 July 2010, Swiss and southern German influence, and (right) 09–11 July 2010 North African and Swiss influence. For plots with higher time resolution (3 h), see http://lagrange.empa.ch/FLEXPART_browser/.

Number concentrations of IN determined were more varied than what we found at Jungfraujoch. In nine measurements, numbers of IN active at −10 °C ranged from 0 to 91 IN m^{-3} (Bowers et al., 2009), nevertheless, the median value (15 IN m^{-3}) was similar to our observation (11.8 IN m^{-3}).

Ice particles formed at warm temperatures (−3 to −8 °C) can multiply in number by rime splintering (Hallett and Mossop, 1974) and at colder temperatures (peak at −15 °C) through ice-ice collisions (Yano and Phillips, 2011). This suggests that precipitation in clouds is not strictly limited by the number concentrations of IN at these temperatures thereby implying that the small number concentrations of IN active at these temperatures can initiate the formation of enough cloud ice to affect precipitation. For example, precipitation rates observed during a 29 day period over the Southern Great Plains have been explained with 10 IN m^{-3} active at −10 °C (Zeng et al., 2009), which is within the range of our observations (2.0 to 15.5 IN m^{-3} active at −10 °C).

3.3 Number of IN per unit mass of PM_{10} depends on air mass origin

Simulated source sensitivities, grouped into three episodes (Fig. 1), indicate different source regions of the sampled air mass. During the first episode (10–11 June) the main origin of the sampled air masses was over Northern Italy, extending south over the entire Italian Peninsula and adjacent Mediterranean to coastal areas in Northern Africa. On 10 June, the weather situation over Western Europe was dominated by a low pressure system over the Bay of Biscay. Several frontal systems were imbedded in the low and influenced the Alpine area towards the evening, causing increased transport from the aerosol laden atmospheric boundary layer. Within Switzerland, convective precipitation was observed both north and south of the Alps but not in the vicinity of JFJ. In the second episode (29 June–1 July), JFJ was influenced by Swiss and southern German boundary layer air that arrived in an air stream that originated over the Atlantic and ascended over England and Northern Germany before recirculating westward over southern Germany. The surface source sensitivities for the third episode (9–11 July) indicate strong local or regional influences, but also considerable sensitivities were simulated for Northern Africa and Spain, suggesting potential dust transport from the Saharan dessert. The apparent Saharan dust episode starts abruptly on 9 July with PM_{10} concentrations (continuous analyser) rising from about 1 µg m^{-3} to 50 µg m^{-3} within 12 h while the mean CO mixing ratio for that day was below average (94 ppb). CO exhibits a latitudinal gradient in the northern hemispheric free troposphere with smaller values towards the south. Thus, decreased CO levels at JFJ are often associated with free tropospheric advection of southern air masses (Bond et al., 2011). In the present case, increased PM_{10} and decreased CO agree well with the advection of Saharan air masses without further surface contact over Northern Italy as derived from the transport simulation. During 10 and 11 July, PM_{10} concentrations slowly returned to 5–10 µg m^{-3} while mean daily CO increased again to about 110 ppb (hourly means to >115 ppb). Especially on 11 July the site received considerable amounts of regional (Swiss) boundary layer air, as we could infer from increased afternoon observations of hourly means of CO, NO_y and absolute humidity, and intensified source sensitivities close to the site.

We have two clearly distinct types of PM_{10} origin. One is the second episode (29 June–1 July), where PM_{10} originated largely from the Swiss and southern German boundary layer. The other type corresponds to the first two days of the Saharan dust event (9–10 July), which was evident also in the ochre colour of the PM_{10} filters. This colouring was much less pronounced on the last day of this episode (11 July), where the filter colour resembled more that of filters from the first and second episode, probably because of the considerable amounts of regional (Swiss) boundary layer air sampled during the afternoon of that day.

Number concentrations of IN per m^3 air were twice as large when air at JFJ was from the Swiss and southern German boundary layer, compared to air dominated by the

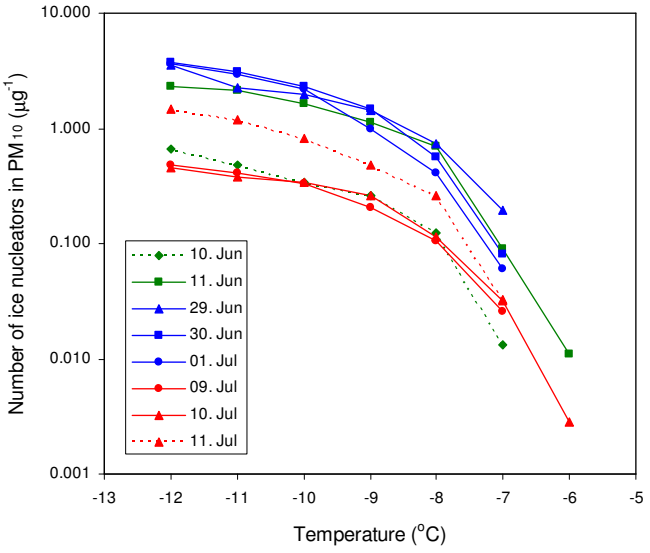

Fig. 2. Number of IN sites per unit mass of PM_{10}, derived from analysis of PM_{10} filters, which had been used to sample air from different origin during 24 h (720 m^3): (blue) PM_{10} originating largely from the Swiss and southern German boundary layer; (red) Saharan dust event, (broken line) with considerable amounts of regional (Swiss) boundary layer air; (green) North Italian influence, (broken line) possibly affected by precipitation events.

Saharan dust event (9–10 July), although the latter events carried a three-fold larger PM_{10} load (Table 1). On PM_{10} from sources north of the Alps there were four times more IN per unit mass of PM_{10} active at −7 °C, and eight times more at −12 °C, compared to PM_{10} from the apparent Saharan source (Fig. 2). These results support, but do not prove until the source of IN are specifically identified, the proposition by Conen et al. (2011) that larger numbers of IN per unit mass of soil dust may be found in cooler regions and where soils have larger concentrations of organic matter, compared to warmer regions or where soils have lower organic matter concentrations, such as desert soils. At the same sampling site (Jungfraujoch), Kamphus et al. (2010) previously analysed single cloud ice residues by time-of-flight-mass-spectrometry. Mineral dust was the dominant ice residue in the mixed phase clouds they had sampled. Soil dust is, together with bacteria and fungal spores, the most likely carrier of IN sites active at temperatures ≥ −12 °C. Pollen grains are also IN active at these temperatures, but are generally larger than 10 µm and, if present, are not collected on the PM_{10} filter. Fragments of pollen are active only at lower temperatures (Pummer et al., 2011). Soot and purely mineral particles display their IN activity mostly at temperatures < −12 °C. When considerable amounts of regional (Swiss) boundary layer air were added to the fading Saharan dust event (11 July), numbers of IN per unit mass of PM_{10} increased to values between those of the Saharan and the Swiss/southern German PM_{10} source.

Air masses mainly influenced by Northern Italy had numbers of IN per unit mass of PM_{10} either similar to air masses from Switzerland and southern Germany (11 June), or as the unmixed Saharan dust events (9–10 July). It may well be that the small numbers of IN on 10 June were caused by IN having been preferentially deposited, compared to non IN-active PM_{10} particles, in precipitation events during that day. This is not unlikely, considering the role of IN in initiating precipitation by the Wegener-Bergeron-Findeisen process.

3.4 Caveats

An obvious limitation of using 24 h samples is that shorter episodic events can not be investigated. Another potential disadvantage of retrospectively selecting PM_{10} filters for analysis is that IN properties may change during filter storage. Living *Pseudomonas syringae*, for example, change their IN activity within hours, depending on temperature and nutrient status (Nemecek-Marshall et al., 1993). IN active sites in organisms are proteins (Wolber et al., 1986; Morris et al., 2004). These are well preserved when sorbed to mineral surfaces (Kleber et al., 2007). Hence, unlike IN associated with living organisms, biological IN sorbed to mineral soil particles should not be affected by prolonged storage. Stevenson (1968) simultaneously exposed ten Millipore filters to the same stream of ground level air, analysed one immediately and the others successively within the following 13 days. She observed no change in the number of IN over this period, which indicates at least a certain stability of atmospheric IN. Our samples had spent about one year in a climate controlled room at 22 °C and 50 % relative humidity before they were analysed. The median number of IN is very similar to that observed by Bowers et al. (2009), who stored their filters at −20 °C and analysed them within the first two weeks following the collection campaign (Robert M. Bowers, personal communication, 4 October 2011). This does not prove that our filters were unaffected by the storage, but it also does not contradict the assumption. Trials over a longer time period are necessary to identify acceptable time lags between PM_{10} sampling and IN analysis.

An advantage of using PM_{10} filters loaded by a high volume sampler is that even a small number of IN m^{-3} can be detected. For the method parameters used here, a single tube frozen of a total of 108 tubes represents 0.08 IN m^{-3} ([ln(108) – ln(107)]/0.12 m^{-3}). However, the high sensitivity also limits the maximum number of IN m^{-3} that can be determined. In our study, it is 39 ([ln(108) – ln(1)]/0.12 m^{-3}). It could be increased by cutting out smaller circles from the filter. Yet there is a practical limit to this because of the felt-like nature of the filter material and its thickness of about 0.5 mm. The smaller the cutting, the shorter are individual fibres in the cutting and the more likely its disintegration before it can be placed into a tube. Even, if it would be possible to cut circles with 1 mm diameter, the maximum number of IN m^{-3} would only be 126. Another way to increase this number

is by increasing the number of tubes, say from 108 to 200, but the effect would only be minor (factor 1.13). Hence, the method is most suitable for the small number concentrations typically encountered at the warmer end of the heterogenous freezing range that is typically occupied by biological IN. For colder temperatures, where in addition to biological particles also clay particles become IN-active, other methods must be employed. Already at $-18\,^{\circ}C$, Klein et al. (2010) observed 1230 IN μg^{-1} PM_{10} during a Saharan dust event sampled at Taunus Observatory in central Germany (825 m a.s.l.), suggesting that there may be a steep IN activation curve versus temperature for mineral dust particles in light of our new results during an episode different from the one investigated by Klein et al. (2010).

4 Conclusions

Monitoring of PM_{10} by a gravimetric filter technique is performed routinely in many parts of the world. Additional information on aerosol chemistry is often available for these stations and can add valuable information on possible interaction of IN with substances that might affect their behaviour. Number concentrations of ice nucleators (IN) in the atmosphere can be derived from the analysis of small parts of PM_{10} filters subjected to drop freeze tests. The technique is limited to small number concentrations of IN, so to the warm end of freezing nucleation spectra dominated by biological IN. Filters may be selected retrospectively from particular stations and for specific events, such as the arrival of air masses from a certain source region. Without additional infrastructure and sampling effort it is possible to study factors affecting the abundance and variability of IN per unit mass of PM_{10}. Together with available data on PM_{10} mass and atmospheric transport, time series of IN number concentrations in the atmosphere may be re-constructed for locations where PM_{10} is monitored by gravimetric filter method.

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