

Number Size Distributions of Submicron Particles in Europe

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Abstract The aerosol particle number size distribution is a key component in aerosol indirect climate effects, and is also a key factor on potential nanoparticle health effects. This chapter will give background on particle number size distributions, their monitoring and on potential climate and health effects of submicron aerosol particles. The main interest is on the current variability and concentration levels in European background air.

The submicron particle number size distribution controls many of the main climate effects of submicron aerosol populations. The data from harmonized particle number size distribution measurements from European field monitoring stations are presented and discussed. The results give a comprehensive overview of the European near surface aerosol particle number concentrations and number size distributions between 30 and 500 nm of dry particle diameter. Spatial and temporal distributions of aerosols in the particle sizes most important for climate applications are presented. Annual, weekly, and diurnal cycles of the aerosol number concentrations are shown and discussed. Emphasis is placed on the usability of results within the aerosol modeling community and several key points of model-measurement comparison of submicron aerosol particles are discussed along with typical concentration levels around European background.

Keywords Aerosol number concentration, Aerosol number size distribution, Atmospheric aerosols, CCN

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1 Introduction

Air quality effects of aerosols have traditionally been studied in accumulation and coarse mode, concentrating largely in the supermicron particle range, usually by using particle mass as the main property of interest (e.g., PM_x). However, submicron particles have also many important effects to both air quality and the climate system.

The health effects of atmospheric aerosol particles are usually characterized by aerosol particle mass concentration in either PM_{10} or $PM_{2.5}$ [1]. Nanoparticles (commonly defined as particles with $D_p < 100$ nm) have been widely acknowledged to have potential for adverse health effects, although the knowledge which particle property is most important for health effects has not yet been generally agreed on [2]. However, the particle deposition to alveolar region of lungs seems to be especially efficient for particles in the size range between 10 and 50 nm [3]. The research on nanoparticle health effects has been recently increased due to the current wide interest in the industrial nanoparticle processes, with obvious occupational health risks. The health effects of these nanoparticles are potentially important also for the public, as concentrations of sub-50 nm particles are known to be high in many areas. For such particles, a major source of urban air concentrations is traffic, usually diesel soot [4]. As an indication of the potential dangers associated with such ultra-fine particles, recent controls for automotive emissions in the European Union include a number emission limit for particles larger than 23 nm in diameter [5].

The climate effects of atmospheric aerosol particles are a matter of continuous interest in the research community. The aerosol-climate effects are divided into two groups: The direct effect represents the ability of the particle population to absorb and scatter short-wave radiation – directly affecting the radiation balance. These direct effects depend primarily on the aerosol optical properties and particle number size distribution, as the particle size significantly affects the scattering efficiency of

shortwave radiation [6]. The indirect effects affect the climate system through the clouds and mostly with the cloud albedo effect and the cloud lifetime effect. The cloud albedo effect (Twomey effect) is the resulting change in cloud radiative properties due to changes in cloud droplet number concentration (CDNC) [7]; the lifetime effect (Albrecht effect) is connected to the changes in cloud properties and in drizzle and precipitation [8]. The aerosol indirect effects are controlled by the ability of particles to activate to cloud droplets (i.e., to be cloud condensational nuclei, CCN) within a cloud [9]. This ability is a strong function of particle size, water supersaturation, and particle hygroscopicity (i.e., chemical composition). An extensive overview of the processes affecting the ability of particles to act as CCN is provided in literature [10], with the conclusion that the particle size is the dominant aerosol property on cloud droplet activation, making particle number size distribution the key factor in aerosol-climate interactions.

1.1 Properties of Aerosol Number Concentrations and Size Distributions

In the submicron range, the aerosol population typically consists of several subpopulations, so-called modes, which are indicative of different loss and formation processes in the atmosphere. The smallest aerosol particles are formed from gas phase vapors via nucleation, forming the nucleation mode. In slightly larger sizes, the Aitken mode particles are produced via growth from nucleation mode and a wide variety of combustion and natural sources. The largest submicron particles are in the accumulation mode, with a major source being growth from Aitken mode, e.g. via cloud processing and condensation. Only the smallest tail of the coarse mode can be seen in the submicron range, and the overall effect of coarse particles in the submicron particle range number concentrations is generally very small. Often as a rough estimate the particles with diameters between 30 and 100 nm are considered to belong to Aitken mode and particles between 100 nm and 1 μm to the accumulation mode. The particle modes can move in the size axis, and they are not always visible in the measured size spectra, especially nucleation mode is often absent during nighttime.

As particle number size distributions can be complex, and the instruments used generate large amount of size distribution data, which can be hard to effectively describe, a common method is to calculate integrated particle number concentrations for specific aerosol particle diameter ranges, depending on which part of the particle number size spectrum is needed for the application. In this chapter, three different ranges are used (Fig. 1a):

- Number concentration of particles between 30 and 50 nm of dry diameter (N_{30-50}), given in particles per cubic centimeter (cm^{-3}). These particles represent smaller end of the Aitken mode particles and are representative of recently emitted or formed nanoparticles, which have high probability to end up in

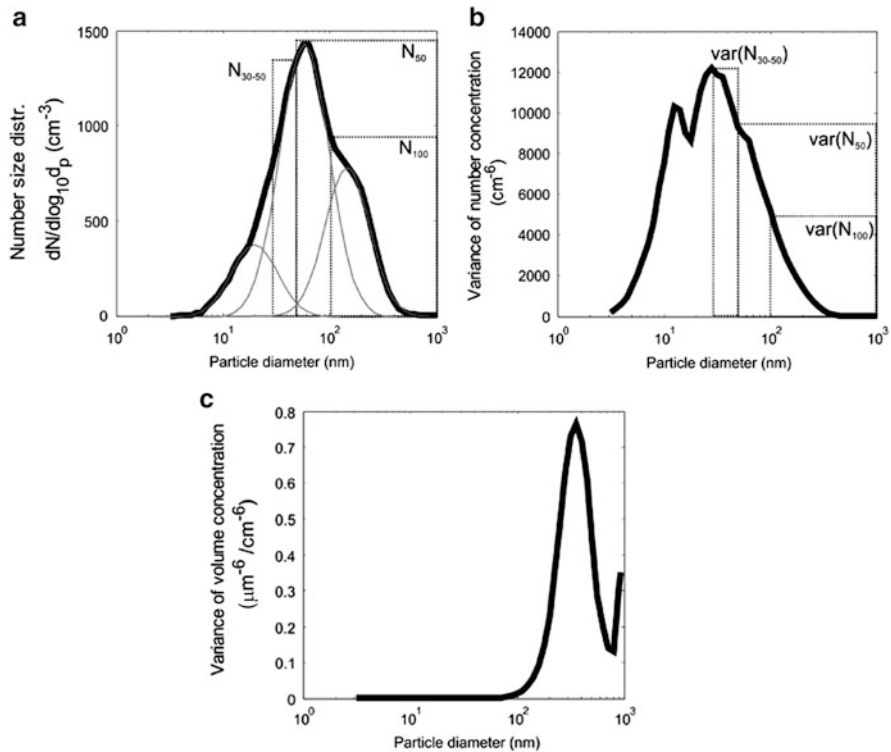


Fig. 1 (a) Typical clean Northern European median number size distribution (measured at SMEAR II station in Hyytiälä, Finland). The approximate modal locations and size ranges of different integral properties of the aerosol number size distribution used are shown; (b) variance of number concentration as a function of particle diameter; (c) variance of (computed) volume concentration in the same station (adapted from Asmi (2012), [11])

alveolar regions of lungs. The smaller diameter limit of 30 nm comes mostly from trying to keep the instrumental datasets comparable. These particles have generally relatively low lifetime (in the order of one or two days) and thus are more representative of the local emissions.

- Particle number concentration between 50 and 500 nm of diameter (N_{50}), which represents particles from larger diameter end (i.e., more aged) Aitken mode, together with the entire accumulation mode. The 500 nm upper limit is due to instrumental limitations. These particles are representative of CCNs for high updraft velocity clouds, as typical aged particles ($\kappa = 0.18$) with 50 nm diameter are activated with water supersaturation of 0.8%. The upper limit of 500 nm is chosen to have comparable values for different instruments. As the particle number size distribution over 500 nm of diameter is usually insignificant in terms of number concentration in comparison with sub-500 nm size ranges (Fig. 1a), making the N_{50} a good representative parameter of the total potential CCN concentration.

- Similar to N_{50} , we also show the number concentrations between 100 and 500 nm in diameter (N_{100}), representing CCNs for lower updraft velocity clouds, and a rough estimate of the number concentration in accumulation mode as the Hoppel minimum between the Aitken and the accumulation modes is often around 100 nm of diameter.

These concentrations in different size ranges give then an approximation of aerosol concentration levels for both air quality (N_{30-50} and lesser extent N_{50}) and for climate applications (N_{50} and N_{100}). The properties are in a sense similar to the mass-based PM_{10} and $PM_{2.5}$ measurements, providing easy way to compare individual concentrations.

1.2 Key Differences Between Number and Mass Measures of Aerosols

The particle number and mass concentrations can sometimes correlate in some timescales, although such behavior should not be automatically assumed. Studies have shown that seasonal correlations between particle number concentrations and mass concentrations in several sites over Europe are high [12]. Thus, there is some indication that if the site is relatively polluted (i.e., PM concentrations are high), the accumulation mode particles are generally high as well. However, in smaller timescales, such as days and hours, these correlations can disappear [11]. The main reasons behind the lack of correlation are the complex dynamics of the particle number size distributions, as larger particles in micrometer range can effectively hinder many particle formation and growth processes, which are crucial to the particle number concentrations. Mass and number are thus different aspects of the aerosol population and should not be considered necessarily similar in behavior.

Number concentrations are dominated by submicron particles, whereas the mass concentrations are strongly influenced by particle concentrations in 0.1–10 μm diameter range [13]. Similarly, the variability of the number-based measurements is strongly dominated by variability in smaller diameter ranges, whereas the variability of mass-based properties, such as PM_{10} , are dominated by variability in the accumulation mode (usually around 500 nm of mass mean diameter) and in the coarse mode. This means the variabilities of these properties are not necessarily similar in shorter timescales, due to sensitivity of variance from very different air masses and thus aerosol types. This is demonstrated in Fig. 1b, where the variance of the each size class of particle number concentrations between 3 and 1,000 nm is shown for SMEAR II station in Hyytiälä, Finland. The variance has similarities to the particle number size distribution (Fig. 1a), but there are also significant differences, especially on smaller particles sizes. Even though in the median particle number size distribution the nucleation mode is visible only weakly, it is a major contributor to submicron particle number concentration variability.

Figure 1c shows the variability of the submicron aerosol volume distribution (calculated from number size distribution using assumption of spherical particles) as the function of size. As the particle volume concentration is closely connected with particle mass concentration, two key findings come apparent: (1) as the aerosol volume variability is dominated by larger accumulation particles in the diameter range from 300 to 700 nm, the variabilities of most mass-based aerosol measurements (especially PM_{10} , as it is not dependent on supermicron coarse mode, but in lesser extent also $PM_{2.5}$ and PM_{10}) are very sensitive to changes in these particles sizes, and in comparison (2) the variability of particle number concentration is rapidly diminishing above 100 nm in diameter, show that the variability of that aerosol number concentrations are not strongly influenced by changes in accumulation mode particle number, and that the used integral particle number concentrations (N_{30-50} , N_{50} and N_{100}) are mostly sensitive to changes in the smallest particle sizes in each diameter range.

In short, the mass-based measurements are often more sensitive to aerosol concentration changes near the maximum diameter of the size range measured, whereas the number-based measurements are more sensitive on aerosol concentration near the minimum diameter measured.

2 Measurement and Monitoring in Europe

2.1 Measuring the Aerosol Particle Number Size Distributions

Two types of particle mobility particle size spectrometers for measuring submicrometer particle number size distributions are generally used: the differential mobility particle sizer (or DMPS), and the scanning mobility particle sizer (SMPS) [14]. Both are very similar instruments in their operation: they aspirate dried air, use ionizing radiation to establish an equilibrium bipolar charge-distribution in the sampled aerosol, use a cylindrical differential mobility analyzer to select particles based on their electrical mobility, and use a condensation particle counter to measure the resulting concentrations in each of the selected electrical mobility. The main difference between these instruments is the mode of operation, as the DMPS keeps the differential mobility analyzer voltage constant during measurement of a single size interval and the SMPS scans with continuously differing voltages. The size range and time resolution of a DMPS or an SMPS system depends on the system architecture (e.g., the physical dimensions of the instrument and the flow rates used) and on user choice (more size channels vs. time resolution). One key factor is that the measured particle properties are measured for *dry conditions*. The sample air is dried to relative humidity $RH < 40\%$ before size selection, meaning that most of the water is evaporated from the particles, and thus they are most likely smaller than in ambient conditions.

Notably, the instruments used in the European Supersites for Atmospheric Aerosol Research (EUSAAR)/Aerosols, Clouds, and Trace gases Research Infrastructure Network (ACTRIS) and German Ultrafine Aerosol Network (GUAN) measurements used in this chapter are from intercalibrated measurements, where the abilities of the instruments were determined in common intercalibration workshops [15]. Overall, the instruments agree well on particle sizes between 20 and 200 nm, with the differences above 200 nm still relatively minor for number concentrations. In smallest particles sizes the instrument deviation is large, and for this reason we only consider particles larger than 30 nm in diameter in this chapter.

2.2 Networks of Measurements in Europe

Several European intensive short-term (“campaign-type”) projects have provided important information on the atmospheric aerosol properties in Europe, usually by concentrating on specific aerosol properties or interactions. However, these kinds of campaign-type measurements do not necessarily represent the seasonal or annual variations of the aerosol concentrations and can overestimate some properties of the aerosol populations. Long-term measurements, especially with intercalibrated instruments and common data handling and calibration protocols make the data comparison between stations much more reliable and provide the end users (e.g., atmospheric modelers) good datasets to compare with.

The EUSAAR project of the Sixth Framework Programme of the European Commission is one of the steps towards a reliable and quality-controlled network of measurements [16]. The EUSAAR project improved and homogenized 20 European sites for measuring aerosol chemical, physical, and optical properties following a standardized protocol of instrument maintenance, measurement procedures, and data delivery in common format to a common database. EUSAAR also provided inter-comparison and calibration workshops as well as training for the station operators. The work started in the EUSAAR is continued in ACTRIS infrastructure of the Seventh Framework Programme of the European Commission.

GUAN is a network of multiple German institutes with an interest in submicron aerosol properties, which was established in 2008 [17]. The methodologies of particle number size distribution measurements and data handling procedures in both GUAN and EUSAAR networks are very similar, and the size distribution measurement results are comparable between the two networks. The EUSAAR measurements were available (with some station-to-station variability) for the year 2008–2009 and the GUAN measurements were mostly from 2009. The locations of the stations are shown in Fig. 2.

A key feature of the EUSAAR and GUAN stations is that they are regional background stations. This means in this context that the stations are expected to represent the (possibly polluted) background air and long-range transport, not the direct influence of any obvious local sources. This means that the levels of aerosol

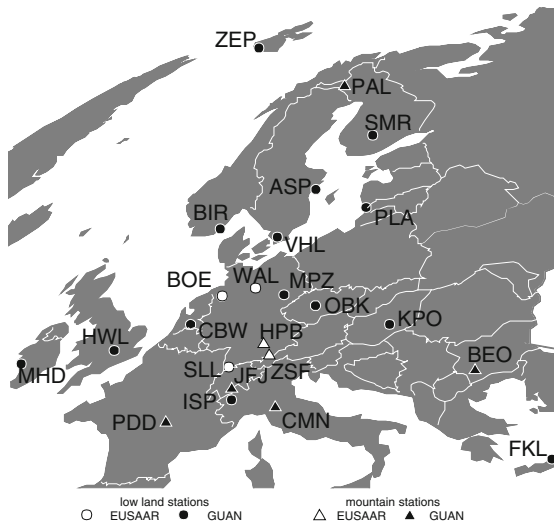


Fig. 2 Stations used in measurements of aerosol number size distributions. *Black symbols* are EUSAAR stations, *white* GUAN (MPZ was in both networks). *Triangles* denote high-altitude mountain stations (over 1,000 m from mean sea level). Figure adapted from figure published in [18], which also has more details on the locations and types of the stations

concentrations measured at these stations should represent the overall regional background concentrations and should be thus representable of a large footprint area around them [19].

3 Levels and Variability of Aerosol Number Concentrations

3.1 General Properties of Number Size Distributions

The particle number size distributions can be, as previously noted, often considered to be a combination of several aerosol subpopulations or modes. These modes are often log-normally distributed in the diameter space. Interestingly, the concentration histograms (i.e., frequency of detecting specific concentration) are typically also log-normal. Thus, using linear measures of concentration or size, such as arithmetic mean, can be strongly influenced by outlier values. This is the reason why either order-based metrics (such as percentiles and medians) or geometric properties (e.g., geometric mean or geometric standard deviation) of distributions are better mean properties to study if one is interested in typical concentration levels or mean particle diameters. The logarithmic occurrence spectrum is not only a feature of particle number concentrations. There are many reasons to expect similar behavior from the particle mass-based metrics [12], even though arithmetic means are the traditional method of averaging in the air quality contexts.

The log-normality of both size distributions (concentration vs. diameter) and in concentration histograms (occurrence vs. concentration) is a product of almost stochastic processes affecting the growth of aerosol populations. Distribution, which has a stochastic growth behavior dependent on the free variable, has tendency to approach log-normal shape [20]. In the case of particle number size distribution, the main growth process is condensation. In the case of particle number concentration, the increasing (or growth) process is both condensational growth from smaller size ranges and emission events. These essentially random growth incidents tend to derive the modes towards log-normal shape both in size and in concentration space. In both cases, the shape of the size distribution is further affected by additional processes, such as coagulation and emissions, which affect the widths and shapes of the distributions, bending and changing the distribution shapes away from log-normality.

Also, the particle number concentration histograms can have multiple “concentration modes.” These can be interpreted as different air masses or emission periods affecting the number and mass concentrations measured at the stations. Such behavior is often seen in locations with time-dependent influence of either very clean air (resulting in a log-normal mode of smaller concentrations) or very polluted air (resulting in a log-normal mode of higher concentrations). Similar multi-modal histograms can also be detected in some cases at stations with high seasonality, where each mode corresponds to a seasonal concentration distribution.

3.2 Spatial Differences and Similarities of Aerosol Number Size Distributions

Combining the physical aerosol measurements from a high number of European background stations shows that there are clear similarities between particle number size distributions and concentration levels measured at different locations over wide geographical regions. These similarities are connected to similar emissions, particle loss processes, and meteorological patterns. The main aim of this section is just to provide key factors of each station categorization, more details and complete analysis of individual stations are available in [18] and references therein.

3.2.1 Central European Background (See Fig. 3)

The particle number size distributions and concentration levels measured at the Central European stations were remarkably similar. The median particle number size distributions did not change significantly from season to season, and the differences between the stations were not very large (N_{50} from 2,500 to 3,100 cm^{-3}). The variability of nucleation and small Aitken particles was elevated

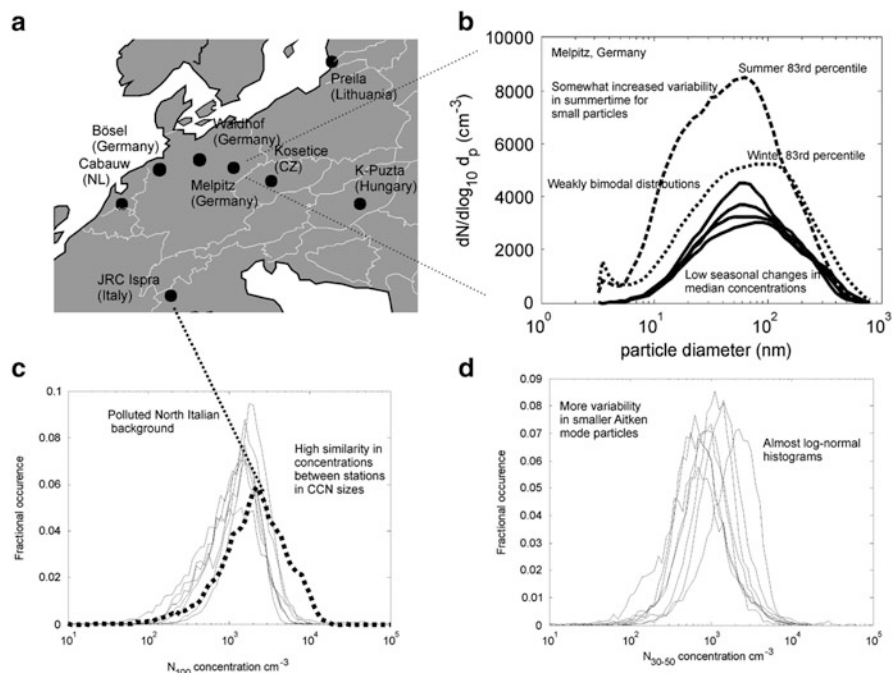


Fig. 3 Key features of submicron aerosol measured at Central European and North Italian EUSAAR and GUAN stations. (a) location of the stations, (b) key features of size distributions, (c) key factors of N_{100} concentration histograms, and (d) in N_{30-50} concentration histograms

on summer and autumn months in some stations, leading to short periods of higher concentrations in number concentrations of particle sizes smaller than 100 nm in diameter.

In the histogram (occurrence) plots, the N_{30-50} concentrations showed in some stations weak seasonality, with wintertime concentrations more likely to have decreased concentrations compared to summertime values. However, in the N_{50} and N_{100} concentrations, no seasonality was detected. The histograms are also unimodal and relatively narrow, which suggests very homogenous environment for all of the integrated number concentrations studied. There is also very little evidence of a strong diurnal cycle in the aerosol sizes studied. The station annual median concentrations of N_{30-50} varied between 410 and 1,120 cm^{-3} , N_{50} between 1,330 and 3,387 cm^{-3} with most stations over 2,300 cm^{-3} , and N_{100} between 739 and 1,863 cm^{-3} . The lack of seasonality may have two major reasons. First of all, the relative contribution of the natural aerosol particle sources is smaller than on more remote stations, and secondly, the overall meteorological situation in Central Europe has less strong influence on aerosol concentrations than, e.g., Northern Italy.

Overall, the results suggest that the particle number size distributions in Central Europe are very similar over very large region, and even though the mean concentrations somewhat vary from station to station, the background air in Europe is homogenous from the aerosol point of view.

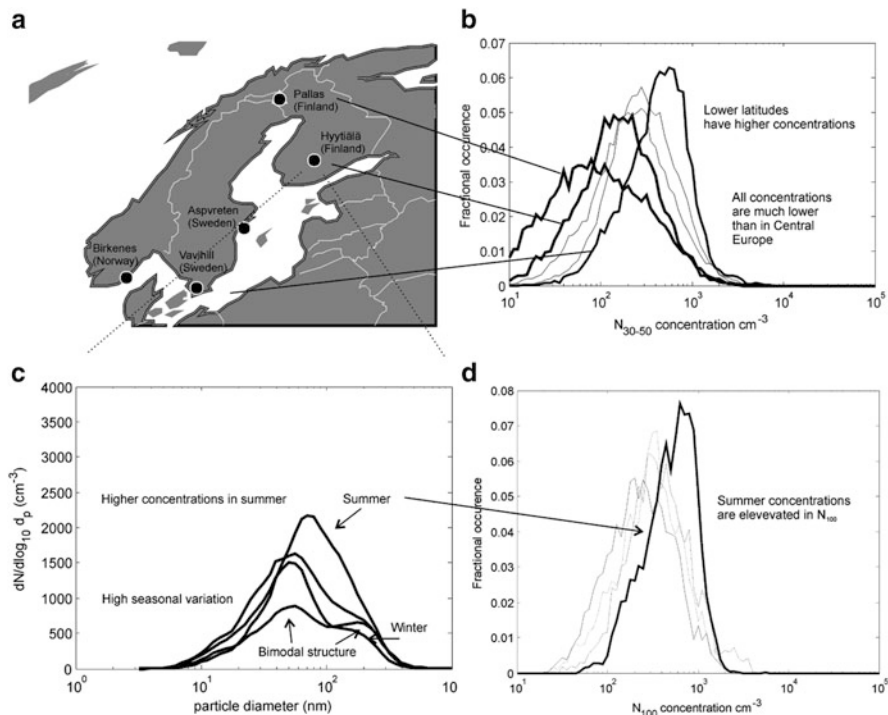


Fig. 4 Key features of submicron aerosol measured at North European EUSAAR stations. (a) location of the stations, (b) histograms of the annual N_{30-50} concentrations, (c) seasonal median size distributions, and (d) seasonal N_{100} variation at Hyytiälä, Finland

3.2.2 Polluted Northern Italian Background (See Fig. 3)

An extreme case of polluted background station was the Joint Research Centre station near Ispira in Northern Italy. Although the N_{30-50} concentrations were similar to Central European stations, the concentration levels in the larger submicron particle sizes were significantly higher, with median N_{50} concentration of $4,448 \text{ cm}^{-3}$. The seasonality of N_{50} and N_{100} particles was also very high, with wintertime median N_{100} concentrations approaching $10,000 \text{ cm}^{-3}$. The station was characterized by a strong anthropogenic influence and wintertime inversions, which trapped the pollution near the surface. These effects lead to extreme episodes with high concentrations in accumulation mode.

3.2.3 North European Background (See Fig. 4)

Northern Europe is characterized by strong seasonal variation in particle number size distributions and much lower overall concentrations than Central Europe. The high seasonality is from a far larger fraction of non-anthropogenic sources

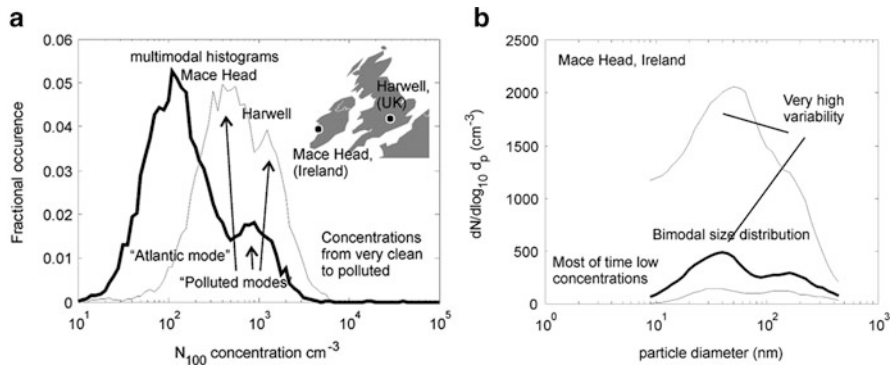


Fig. 5 Britain and Ireland aerosol overview (location shown in the *inset*). (a) Histograms of N_{100} concentration in both stations, (b) Mace Head size distributions, showing 16th, median (*thick line*), and 83rd percentiles of size distribution functions

influencing the size distributions. Although the similarities between the stations are not as obvious as in Central Europe, the datasets have uniformity in regard to seasonal and size distribution behavior. The winter number concentrations are usually lowest, especially for smaller (diameter less than 100 nm) particle sizes. The seasonality also affects the observed differences of day- and night-time values due to differing length of day in the northern latitudes. All of the stations showed bimodal median particle number size distributions, with clear Aitken and accumulation modes. The concentration distributions on some stations show multiple modes, suggesting a combination of more polluted air masses and cleaner air from the Arctic or Atlantic oceans.

The CCN-sized particle number concentration histograms of the Nordic stations are similar for both N_{50} and N_{100} . The stations in general had greater concentrations in summertime, although the concentrations were also elevated during spring in some stations. Northernmost Pallas station concentrations have a very wide histogram, especially in wintertime, suggesting a wide range of sources affecting the concentrations observed at the station. The seasonal variations in CCN-sized particles are large at almost all Nordic stations.

3.2.4 Britain and Ireland Background (See Fig. 5)

The two EUSAAR/ACTRIS stations in the Britain and Irish stations show not only a significant inter-station variability, but also many similarities. The stations have high seasonal variation and large variance in intra-seasonal concentrations. The station data show a prominent spring–summer maximum in all sizes from 30 to 70 nm. The variability was probably due to occurrences of both clean Atlantic and polluted local air masses, and the maximum value at Mace Head during summer months can be attributed to enchanted marine biota activity, which increases the sub-micron particle mass concentration of non-seasalt sulfate and organic aerosol [21].

The histograms show a clear influence of multiple aerosol sources (clean and polluted) and with a high seasonal cycle for smaller particle sizes. Both stations have a very widely spread histogram in all seasons suggesting high variability in concentrations and multiple types of air masses. Most of the Mace Head N_{100} histogram is located at low concentrations with approximately $200 \text{ particles cm}^{-3}$, but with a second mode at about order on magnitude greater concentrations. This is well in line with previous studies from the both stations showing the importance of the difference between air masses arriving over the relatively clean Atlantic Ocean contrasted by polluted air masses arriving from Britain and mainland Europe [22, 23]. Neither of the stations have strong seasonal signals in CCN-sized concentrations.

3.2.5 Mountain Stations (See Fig. 6)

At high-altitude sites (defined as measurement height approximately 1,000 m above mean sea level, note that the categorization is slightly changed from [18] to include some of the intermediate-height stations), particle number size distributions are similar, even though the stations are located in different parts of the continent. The particle number concentrations were low compared to nearby lowland sites, as most of the aerosol sources are on surface. The particle number size distributions generally show bimodal behavior, although the modes are overlapping at some of the stations. The seasonal cycle is similar at all sites, with greater concentrations during summer, especially for particles over 70 nm in diameter. The variability is considerable especially in summertime, suggesting a range of different types of air masses – most likely boundary layer air during daytime and clear tropospheric air during nighttime. Overall, the concentrations are smaller the higher the station is located.

All of the N_{30-50} histograms at mountain sites have similarities, with almost log-normal shapes, with clear concentration tails towards greater concentrations and similar seasonal cycles. The winter conditions, probably more representative of the free troposphere, were characterized by lower concentrations. The summertime histograms show greatest concentrations, probably due to the planetary boundary layer and/or valley winds influence. The greatest concentrations were generally observed during daytime. The median concentrations of N_{30-50} varied between 79 cm^{-3} for Jungfraujoch station in Switzerland (JFJ, altitude 3,580 m) and 418 cm^{-3} for Schausisland (SSL, altitude 1,210 m).

For the N_{50} and N_{100} particles, in most mountain sites the greatest concentrations were observed during daytime summer and autumn. This daytime effect could be connected with air masses arriving from lower altitudes bringing more polluted air from below [24]. The concentrations are all strongly skewed towards lower concentrations. The lowest concentration tails of the distributions are probably indicative of concentrations of the free tropospheric air. The concentrations of the stations with highest altitude had a more pronounced clean mode with N_{100} concentrations below 100 cm^{-3} .

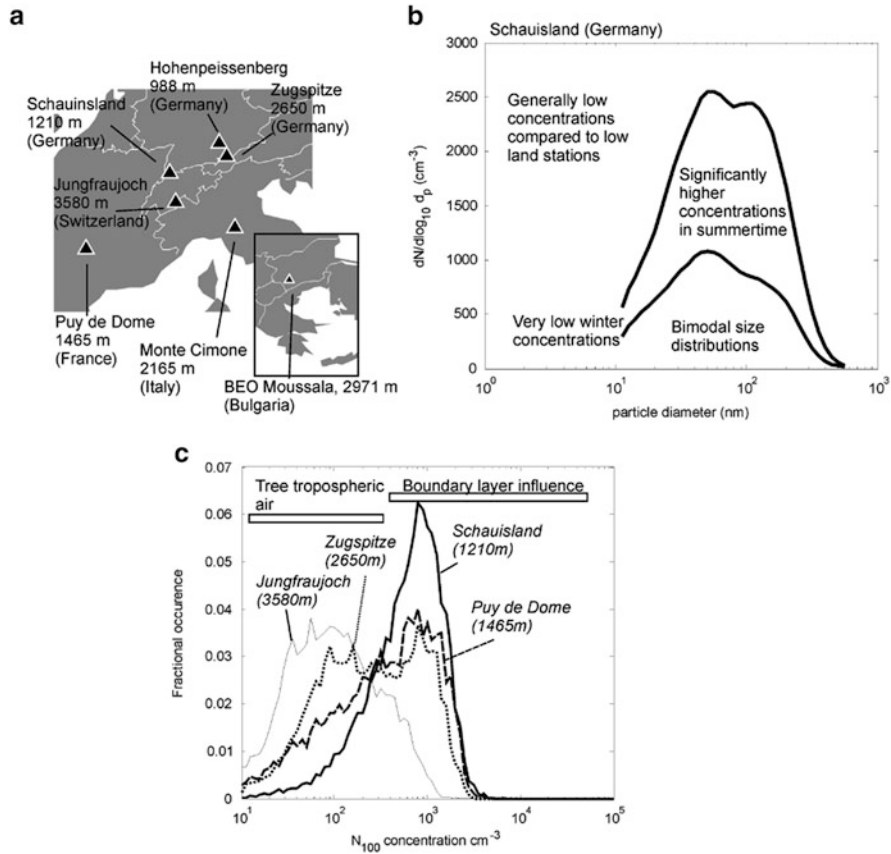


Fig. 6 Features of mountain stations. (a) Location of the stations with their height from the mean sea level, BEO Moussala in Bulgaria is shown in an *inset*, (b) median summer and winter size distributions in Schauinsland showing typical features of mountain size distributions, (c) histograms of N_{100} concentrations in four mountain stations, showing the prevalence of cleaner “free tropospheric” air in the stations located in high locations

3.2.6 Specifics of Arctic Size Distributions (See Fig. 7)

One of the stations, Zeppelin (ZEP), is located far north of the European mainland, on the Svalbard archipelago, 78°N. This far northern position creates many environmental drivers for the aerosol size distribution, almost never seen at the more southern stations. As the station is located north of the northern polar circle, the station is good part of the year in complete daylight (midnight sun), and in complete darkness (polar night). Although the data quality was not always optimal, some indication of the aerosol number size distributions can be made.

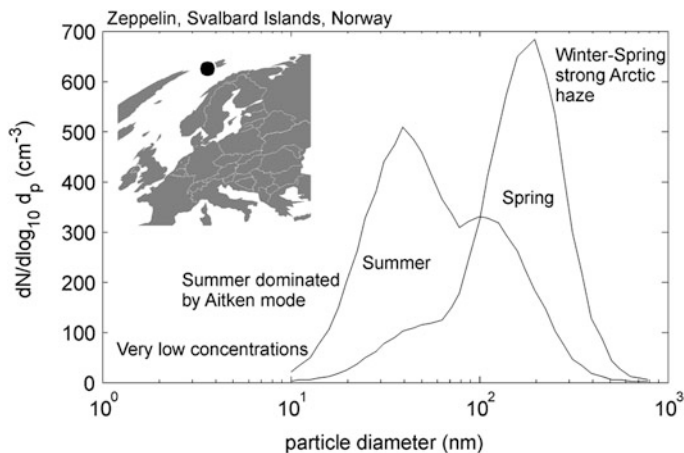


Fig. 7 Features of Arctic station Zeppelin size distributions. Location of the station is shown in the *inset*

In addition to changes in light, the changes in sea-ice and general Arctic circulation make the number size distributions observed at the station very different from southern locations. During winter and autumn, the particle number concentrations were very low with their maxima at around 200 nm. The springtime distributions are dominated by Arctic haze, strongly increasing the concentrations in accumulation mode. In summertime, the distribution changes to very clean marine bimodal distribution, with a strong Aitken mode around 30 nm. This seasonal change is connected to different meteorological situations, daylight as well as changes in ocean ice cover. Concentrations at ZEP were very low compared to European mainland concentrations. The key feature of the Arctic aerosol is the extreme seasonality. During summertime, the particle number size distributions are dominated by a strong Aitken mode, whereas in the winter–spring seasons, a strong accumulation mode is completely dominating the size distributions.

The summertime N_{30-50} concentrations of around 10 cm^{-3} are high, compared to concentrations of around 10 cm^{-3} in other seasons. At CCN-concentrations, a completely different behavior can be seen, as the, e.g., N_{100} concentration is during springtime close to 800 cm^{-3} , in comparison with summertime median of 200 cm^{-3} . The day/night cycle at the ZEP station is very strongly connected to the seasonal cycle.

3.2.7 Eastern Mediterranean Background (See Fig. 8)

At the Mediterranean station Finokalia (FKL) located in the Greek island of Crete, the particle number size distributions were bimodal for winter with an Aitken mode around 50 nm particle diameter and accumulation mode at 150 nm. The spring and summer were dominated by strong accumulation mode at around 100 nm.

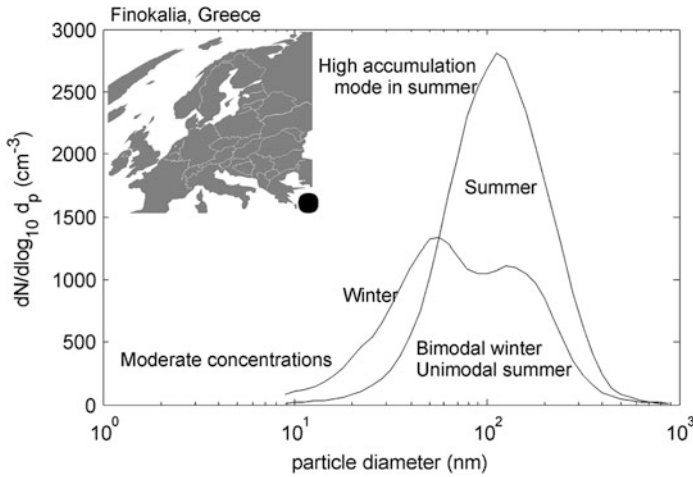


Fig. 8 Features of Eastern Mediterranean Finokalia size distributions. Location of the station is shown in the *inset*

The station had greatest N_{30-50} concentrations during spring and winter with no apparent day/night difference. The concentration levels were relatively low, with a median concentration of 220 cm^{-3} .

The particle histograms show peaks in N_{50} and N_{100} concentrations during spring of over $1,000 \text{ particles cm}^{-3}$. Another smaller mode of low concentrations was also visible around $500 \text{ particles cm}^{-3}$ in both N_{50} and N_{100} .

3.3 Correlations Between Aitken and Accumulation Mode

Figure 9 (adapted from [18]) shows some of the typical correlations between particle number concentrations between 30 and 100 nm (here referred to as “Aitken mode,” although a more rigorous derivation would require actual modal fitting) and concentrations between 100 and 500 nm (“accumulation mode”). The idea of this kind of plot is to show the possible correlation between the two aerosol modes, to identify some of the main particle number size distribution types, and whether the particle number concentrations in both modes increase in the same rate.

In general, the Aitken and accumulation mode number concentrations are correlating (on logarithmic scales), but on different environments, the correlation is not always along the 1:1 line. Aerosol at the Nordic, Mediterranean and polluted continental (Central European) conditions has roughly distributions along the diagonal, which shows that in most cases the Aitken and accumulation modes are behaving in the same way. This suggests that the shape of the particle number size distribution is relatively nonsensitive to the overall concentration levels. In contrast, the free tropospheric part of the mountain distributions is almost round in shape, a

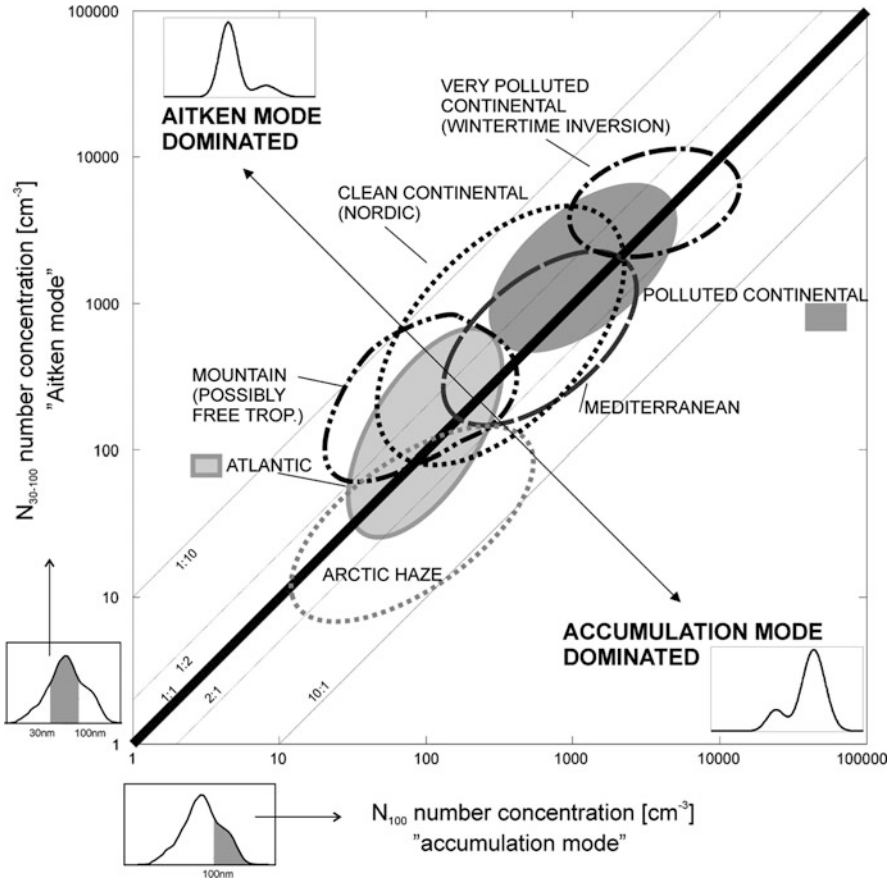


Fig. 9 Typical ranges of Aitken and accumulation mode number concentrations (separated by 100 nm dry diameter) in different European environments. The areas show the densest parts of the different environment concentration scatter (see Asmi et al. [18] for details, adapted from the same article)

sign that the two modes are relatively non-correlated in these air masses. In the case of Atlantic and polluted Italian background, the two modes are correlated, but not in diagonal direction. Atlantic air masses seem to increase in concentration mostly in Aitken mode, suggesting that most of the variability is in sub-100 nm range. The polluted background environments instead have a strong increase in accumulation mode, with relatively low variability in Aitken mode. Only Arctic haze environment has very strong dominance of the accumulation mode, although considerable parts of most other environments sometimes show such behavior.

Overall, in most environments the two modes are correlated, but different environments have very varying concentration levels of the two modes (see Table 1), and their relationship varies strongly from environment to environment and has relatively large scatter.

Table 1 Representational (geometric) mean aerosol number concentrations in European background environments (data from [18])

Environment	Typical particle number concentration between 30 and 100 nm (cm^{-3})	Particle number concentration between 100 and 500 nm (cm^{-3})	Spatial variability
Central European polluted background	1,500 (400–8,000)	1,000 (400–6,000)	Low
Northern European background	800 (80–5,000)	400 (50–2,000)	High
Atlantic air masses on Britain and Ireland	200 (30–700)	100 (30–300)	High
Eastern Mediterranean sea	800 (200–2,000)	700 (100–3,000)	Unknown (1 station)
Mountains (probably free tropospheric)	100 (20–700)	100 (20–400)	Smaller concentrations on higher sites
Arctic Haze period	40 (8–100)	80 (10–500)	Unknown (1 station)
Polluted inversion (Northern Italy)	5,000 (2,000–10,000)	3,000 (800–10,000)	Unknown (1 station)

The values in parentheses give the approximate typical variability range, including the spatial and temporal variability

3.4 Short Scale Temporal Variability

Sub-seasonal differences in particle number size distributions can come from many sources. In very short timescales, the spatial variability of local sources, atmospheric turbulence, cloud processing, precipitation, and other short-time variabilities can create significant differences in particle number size distribution. Diurnal cycles can also be important for the particle number size distributions, as the differences in emissions or mixing layer heights can lead to changes in particle mass and number concentrations in the surface layer. In Central European stations, the differences between day and night concentrations were not large, but some indication of the highest concentrations occurring more likely in the nighttime could be detected, especially for N_{100} . This behavior was much stronger in polluted Northern Italian station, further suggesting the meteorological background of the high concentrations in larger particle sizes. For the Northern European (excluding Northern Lapland Pallas) mountain and Britain and Ireland sites, no such strong diurnal effect could be found. The strongest day/night differences were observed in Pallas station (PAL in Fig. 2) in Northern Finland, and (with some reservations in data quality) in Arctic Zeppelin (ZEP) stations, although in these stations, the observed differences do not come from actual diurnal cycles, but from the fact that the stations are located north of the Polar Circle, meaning the strong difference between daytime and nighttime concentrations is actually an artifact of the seasonal variation.

Of particular interest are the differences between days of the week. The so-called “weekend effect” cycle in aerosol–weather interactions is based on observations of day of the week-related variations of meteorological data [25]. These effects have been connected to similar variations in particle mass concentrations and optical thickness detected at measurements sites in urban and suburban and remote locations [26]. The key point of the “weekend effect” is that the weekday-related changes in anthropogenic emissions of aerosol particles could change the regional meteorology in such an extent that the precipitation and air temperature could be significantly affected. This could then have implications on, e.g., weather prediction. The main mechanism behind this proposed weekend effect could be (semi)-direct or indirect aerosol effects. As this could be a direct anthropogenic influence to the short-term weather systems, such existence of such phenomena would influence many atmospheric fields.

As discussed earlier, the indirect effects of aerosols are controlled by the number of CCN, not by aerosol particle mass or optical properties used in many weekend-effect publications. The datasets of CCN-sized aerosol number concentrations in EUSAAR/ACTRIS and GUAN stations do not support indirect effects as a major contributor to the (possible) weekend effect. Figure 10 shows distributions (25–50–75th percentiles) of each weekday in a long time series of two stations. The statistical tests and wavelet frequency analysis could not detect any consistent statistically ($p < 0.05$) significant differences in CCN-sized number concentrations in annual or seasonal datasets from the stations. This means that the concentrations are not generally different in different weekdays, making a strong continent-wide weekend effect unlikely to occur from aerosol indirect effects. The main reason for the differences between number and mass-based weekday variation is probably a combination of different sources and the fact that mass-based measurements measure particles with much lower lifetime [11]. As lower lifetime particles can be removed efficiently from the atmosphere during the lower emission period, the weekday signal for such aerosol properties is larger than for most CCN-sized particles.

Even though there is no significant change in the CCN number concentrations between days of the week, this is not yet the complete picture of potential aerosol-cloud weekend effects. There are many other potential aerosol processes, such as semi-direct effect, which could have significant effect on the local meteorology. Also, the CCN number concentrations have a weak weekday variation within the cities, which could then lead to meteorological weekend effect directly above the urban environment. However, as the urban or semi-urban areas cover spatially quite small area of the Europe (around 5%) [27], the weekend effect is then of much more a local effect, if it exists at all.

The difference between mass and number-based metrics in weekly variation is a good example on the short-time scale differences between the properties. One should be careful on generalizing correlations from long timescales to small timescales, especially near the lifetime of the particles in question.

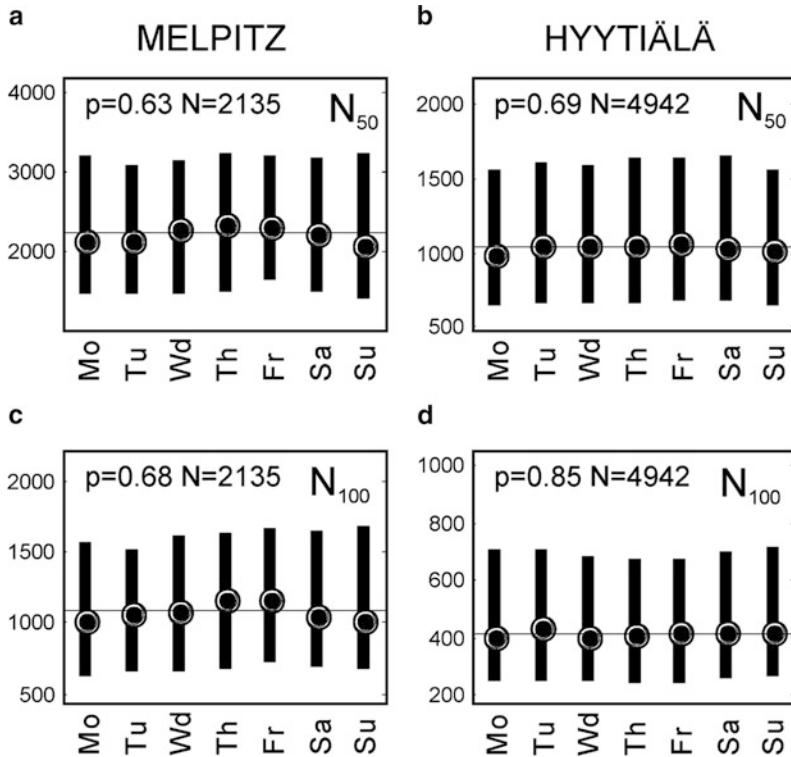


Fig. 10 (a–b) Weekday variation of the N_{50} concentration in Central European background (a, Melpitz, Germany) and in Northern European background (b, Hyytiälä, Finland). *Dots* indicate median concentrations (cm^{-3}) and the *bars* show the variation between 25th and 75th percentile. The p values represent the possibility that all of the weekday distributions are from the same distribution as a result of a U-test. The period of measurements in days is given as N . (c and d) same for N_{100} concentrations. Adapted from [11]

3.5 Comparing Measurements of Number Size Distribution with Model Output

One of the main uses of comparable size distribution dataset is model-measurement comparison. Without comparable data, the air quality and climate models do not have a way to reliably validate their results. In model-to-measurement comparison, many application-based conditions must be taken into account, and especially for aerosol number size distribution, some of the key points are [18]:

- The comparison must be done with similar properties (STP conditions ($T = 293.15 \text{ K}$, $P = 101,300 \text{ Pa}$), dry aerosol).
- Similar timescales for comparison. Short-term simulations can provide easily different or similar particle number size distributions than measured, just from overall model internal variability.

- Longer datasets give possibility to compare distributions of concentrations (distribution statistics, histograms), which give better view of concentrations, processes, and variability than short-term comparisons.
- Multiple peaked concentration histograms are usually a sign of multiple types of airmasses arriving to the station. The model ability to produce all of the peaks is also dependent on capturing correct advection.
- Particle number concentrations in different sizes in the submicron range are strongly interrelated. Comparing just one size range can give too optimistic view of the model performance and multiple size range comparison is useful in pinpointing the processes needing improvement.
- It is worthwhile to consider the special environments of some of the stations. In Arctic, the Arctic haze, in mountains, the transport from lower altitudes and the common inversion situations in Northern Italy can lead to very hard to reproduce size distributions, at least in large spatial scale models.

The EUSAAR/ACTRIS and GUAN data together with some of the analyses is available freely for model-to-measurement comparison uses at <http://www.atm.helsinki.fi/eusaar/>.

4 Conclusions and Outlook for the Future

The submicron aerosol populations in the European background air are variable from location to location. The concentrations and variability of aerosol distributions do, however, show similarities over large geographical areas (Fig. 11). The particle number concentrations are generally lower in more northern and higher mountain locations, naturally as they are generally located farther from the emission areas.

Standardized long-term measurements provide reliable information on statistical behavior of atmospheric aerosols, far beyond what could be obtained in short-term campaign-wise measurements. Although data from a period of only two years is shown, the results already provide a previously unavailable variety of information on the sub-micron aerosol physical properties and variability in Europe. Such information would also be hard to achieve based on information collected from separately managed stations, especially if the instrumentation and data handling are not harmonized.

The similarities within the regions give a good chance of useful air quality model-measurement comparisons. The actual choice of what should be used for the models to compare with depends on the application and complexity needed. The most straightforward way is just to compare one or more mean parameters, such as median concentrations. This approach is simple to do, but can easily lose many features of the data, and, in cases of strongly bimodal histograms, can even be misleading. Comparing modeled histograms to results should pay attention to the histogram mode location (mean or median concentration), width, and relative abundance (height) of each mode in the histograms.

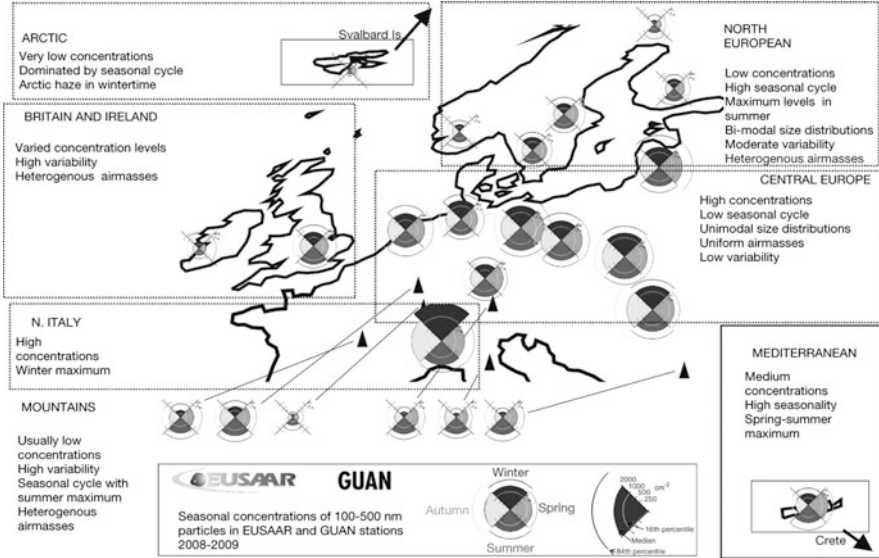


Fig. 11 Overview of submicron aerosol number concentrations. The *symbols* indicate the typical concentrations, variability, and seasonality of N_{100} particles. Adapted from [18]

The EUSAAR/ACTRIS and GUAN networks are globally unique both in data quality and relatively dense network. Building a similar global network is a major undertaking, but would enable the community to efficiently characterize the aerosol number distribution, and thus to improve the potential of characterizing the climate impacts of aerosols in the global boundary layer.

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