Number concentration characteristics of ultrafine aerosols (atmospheric nanoparticles / aitken nuclei) during 2008 over western Himalayan region, Kullu-Manali, India

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The ultrafine particles of three sizes 200, 30 and 10 Å [20 nm (aitken mode), 3 nm, 1 nm (nucleation mode / nanoparticles)] were monitored with water based condensation particle counter during January-December 2008 at Mohal in Kullu-Manali area of North western Himalayas. The results indicate that diurnal pattern has faint bimodal structure with two peaks, one in morning and other in evening but is not as distinct as found in plains. There is rather constant particle density pattern consistent with vehicular movement from morning till evening. This may also be due to abnormally large bursts of particles (nucleation bursts) which are found to be more in summer than winter, more during sunrise and less during afternoon. The weak nucleation bursts are found to be frequent throughout the year than very strong nucleation bursts which are mostly found during months of June, July and August. The monthly 24 h average density gradually picks up from January, increases rapidly in summer months and then decreases in winter. The density is more in summer than in winter, a trend opposite to plains, may be due to development of warm thermal layer on valley floor while cold layer developed along snowy hilltops in winter leading to convection of fine particles up the slopes of valley during daytime. The relatively more value in September and October is due to month long international Dussehra festival in the valley and unexpected lower values in November and December may be due to low local as well as tourist traffic flow; washout/rainout effects; and higher inversion layer. The vehicular survey conducted agrees well with diurnal, monthly as well as yearly averaged diurnal variation of fine particles. The annual average of 24 h average value of ultrafine particles of three size range is 18045±1212, 16811±2790, and 15407±3109 N cm⁻³, respectively. The comparison with earlier results shows significant increase of ultrafine particles indicating impact of vehicular increase in the region.

Keywords: Ultrafine aerosol density, Nucleation bursts, Nanoparticle concentration, Aitken nuclei concentration

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1 Introduction

The study of ultrafine particles is one of the important aspects of Aerosol Science at a particular place, as the impact of these particles on health and climate change are scientifically proven the world over. Further, this study in Himalayan region of Kullu-Manali is of particular interest as the ecology of Himalayan is under serious threat from various forms of pollutants1,2. Himalayan glaciers are receding; 44 snow lakes swollen only in Nepal and Bhutan part of Himalayan region; and biggest river systems of which Himalayan glaciers are source will dry up by 2035 if environmental degradation continues at present pace3,5. This can lead to starvation and wiping of 2.5 billion people living in the drain system of these rivers. Moreover, the environmental factors of hill areas are used as background levels for urban environments. The region specific and season specific studies of ultrafine aerosol characteristics and significance of these characteristics are required to be done in Himalayan region6.

The Indian Space Research Organization - Geosphere Biosphere program (ISRO-GBP) is a step in this direction but it mostly covers urban/semi urban, oceans and coastal areas7. Further, it mainly focuses on aerosol optical depth (AOD), Angstrom parameters, trace gases and radiation budgeting while studies on ultrafine particles are being done at fewer stations and in hilly Himalayan regions of India, this study is non-existent8,9. The anthropogenic activities such as increasing vehicular traffic due to increased tourism related activities, biomass burning, forest fires, cow dung and fuel wood burning for cooking may alter the pollutants level in the region.
Particles in ambient air have size spanning from few nanometers to 100 µm\textsuperscript{10-11}. These particles of various sizes are generated by different sources in atmosphere and rapid process of recombination, nucleation, etc. take place in atmosphere. There are two types of particles in atmosphere: (i) primary aerosols, which are directly produced in atmosphere by wind blown dust, soil erosion, bubble bursts, volcanic eruptions and human activities; (ii) secondary aerosols, which are produced by nucleation of low volatile gases and are mainly produced by industrial activities, forest fires and vehicular emission, etc.\textsuperscript{12} The smallest particles in atmosphere having size less than 20 nm (nanoparticles) are product of various gas-to-particle transformation leading to formation of newborn nuclei (nucleation) which grow by condensation, coagulation and chemical reaction on their surface. These processes are continuously going on in atmosphere and usually have low rate but at some favourable atmospheric conditions, the formation of these atmospheric nanoparticles occur with quite high rate called nucleation bursts (NB)\textsuperscript{13}. Secondary aerosol formation via nucleation of atmospheric vapours is a global phenomenon proven to take place in a wide variety of environments\textsuperscript{14}. Several laboratory and field studies suggest that water, sulphuric acid (via SO\textsubscript{2}), ammonium sulphate, NO\textsubscript{2} and organics clusters are likely participants in atmospheric nucleation and growth\textsuperscript{15-17}. Despite the fact that frequent nucleation bursts has been observed in various locations in the atmosphere, the detailed formation mechanisms and the chemical composition of vapours participating in this particle formation processes remain unclear due to lack of direct atmospheric measurements\textsuperscript{18}. So, the exact mechanisms how particles are formed from precursor vapours are still under debate. The photochemical process in daytime, temperature, humidity, dynamics of atmospheric boundary layer, anthropogenic activities (traffic, industry, burning) and advection of air mass to a particular place are some possible triggering or controlling factors\textsuperscript{19} for the nucleation process at that place.

The particles of size >1 µm called coarse or super micron particles are mostly generated\textsuperscript{12} by dust resulting from excavation, blowing wind, etc. The particles >2.5 µm are generally removed by upper respiratory tract\textsuperscript{20}, called respirable suspended particulate matter (RSPM) and are not much harmful to health. The suspended particles of size less than 1 µm are called fine or submicron particles\textsuperscript{21}. They are further classified as accumulation mode (1-0.1 µm) and fine particles of this range are dangerous as they penetrate in to lungs and produce respiratory problems\textsuperscript{22-24}. The still finer particle of size ranging from 0.1µm to few nanometer called ultrafine (0.1 - 0.01µm = Aitken mode\textsuperscript{25} and 0.01-0.001µm = nucleation mode\textsuperscript{12}) are most lethal to health as they penetrate deep into lungs during inhalation and may even act as nano antibiotic to kill human cells\textsuperscript{26}. The nucleation mode particles are produced mainly through gas to particle conversion and slowly grow by condensation and coagulation into Aitken mode and further into accumulation mode\textsuperscript{19}.

The study of these so called ultrafine or atmospheric nanoparticles or Aitken nuclei is generating more and more interest in scientific community the world over as most of these studies have revealed that particles originating from anthropogenic sources have size less than 2.5 µm\textsuperscript{27-28}. The concentration of these particles around biotic component of earth is not only detrimental to their health but is also important from point of view of particle translocation around human brain resulting depression, anxiety and many other neurological effects\textsuperscript{29-32}. The effects of ultrafine particles including respiratory health\textsuperscript{33}, visibility reduction\textsuperscript{34}, deposition to surface\textsuperscript{35} and severe neurological disorder\textsuperscript{36} depends on particle size. In this communication, number density studies of ultrafine particles and their correlation with vehicular traffic conducted over Kullu-Manali area during January-December 2008 have been presented.

### 2 Site descriptions

The study area Mohal (31°54’N, 77°07’E, 1154 m asl) is flat region lying in middle of the Kullu valley, which is a soap dish type of valley flanked from all sides by mountains of considerable height ranging 3000 – 5000 m. The site is located on valley floor which facilitate it to develop lower nocturnal temperature inversion layer (IBL) in summer and higher snow covered mountain tops in winter, a trend opposite to plains\textsuperscript{37}. The river Beas flows longitudinally through middle of valley and national highway (NH-21) is about 100 m from experimental site. The native population\textsuperscript{38} of area around experimental site is 18,306 while the population of entire Kullu valley which constitutes Kullu and Manali subdivisions of Kullu district, part of Sadar Division of Mandi District, is 221,858.
According to regional transport office (RTO) data there are about 30,000 vehicles of all kinds including two wheelers registered till date and every year about 1,000 vehicles are registered at each subdivision of this valley. The vehicle survey conducted on one of main highway NH-21 during 0600–1600 hrs LT indicate that on average about 5,000 vehicles ply on it every day while there are four other state roads in valley having less traffic intensity.

Being an important tourist place of north India, thousands of tourists flock to Kullu-Manali area of Himalayas during summer. In winter, local anthropogenic activity is low but tourist traffic is increasing as compared to previous years. It increased from 0.13 million in 2004 to 0.55 million in 2008 according to District Tourism Officer (DTO Kullu at Manali, H P, India). The study area, namely the Kullu valley, has experienced tremendous growth in tourism over last decade as tourist diverted to this peaceful shrine region due to adverse condition in Kashmir. It is also evident from the fact that the total tourist traffic to entire state of HP increased from 6.55 million in 2004 to 9.75 million in 2008 (ref.40) out of which Kullu Manali alone hosted 2.12 million tourists in 2008.

The Kullu valley is rain shadow belt having mostly rain during winter months. The heavy snowfall is witnessed in winter months on adjoining hills and once or twice it falls at bottom of valley also. In 2008, there was snowfall in the valley during 21-23 January. The climate of region has three distinct seasons: summer (March to June); rainy (July to September); and relatively longer and harsh winters (October to February). Figure 1 shows meteorological conditions of site retrieved from automated weather system (AWS) present at the institute. The average temperature during measurement days of 2008 increased from 8°C in January to 26.2°C in July and thereafter, it decreased to 10.7°C in December. The wind speed seems to decrease gradually from 0.7 m s⁻¹ in January to 0.4 m s⁻¹ in December with relatively more windy days in February and September. The wind direction is mostly south–west (from Indian plains) throughout the year. It shows gradual increase from 202° in January to 256° in August showing abrupt decrease to 215° in September and thereafter, again increased to 252° till December. The humidity shows decrease from 54% in January to 47% in March and then it increased gradually to 80% in August, thereafter, it again decreased to 55% in December. There has been less rainfall in first half of 2008, i.e. January to July while later half, i.e. August to December witnessed good rainfall. The sunshine duration has been more in first half than in later half of 2008. The present study has been initiated keeping in view the increasing pressure of tourists and other related activities such as forest fires, hydropower excavation works, etc. in western Himalayas.

3 Materials and methods

Regular measurements at every hour from midnight to midnight for various months of 2008 were taken using Condensation Particle Counter (CPC) (Poll-tech Instruments) that can count particles of three sizes: 200 Å (20 nm or 0.02 µm); 30 Å (3 nm or 0.003 µm); and 10 Å (1 nm or 0.001 µm). As the hygroscopic nature of aerosol particles is size and composition

Fig. 1 — Meteorological conditions during CPC measurement days of 2008 at experimental site
specific, it was found that even non-hygroscopic aerosols exhibit response to condensation at increasing humidity\textsuperscript{41} so humidity above 85% is maintained in this instrument. It is well known that urban and continental air is rich in non-hygroscopic particles while hilly and marine air is mostly full of hygroscopic particles\textsuperscript{42} and polluted sites usually have large fraction of non-hygroscopic particles than remote pristine sites\textsuperscript{19}. Also, the efficiency and cut sizes performance for silver, ammonium sulphate and sodium chloride by water based CPC are better than butanol based CPC under increased streamline flow and condition of super saturation\textsuperscript{43,44}. So water based CPC was used for the present study. Upon condensation these particles grow in size leading to fog formation. The degree of fog gives a measure of particle concentration.

Particle Counter Model PEM-PC2 (Fig. 2) is an advanced microprocessor-based instrument, which is user programmable to facilitate automatic measurement and direct display of the number of particles per unit volume of the sampled air. PEM-PC2 utilizes the well-known fact that under suitable operating conditions of super saturation, small particles have the ability to act as condensation centers for water vapour.

The particles from the atmosphere are sampled into the sampling chamber where moist blotting paper provides the saturated atmosphere. Adiabatic expansion of the air due to sudden connection of the sampling chamber to the evacuated auxiliary chamber through the quick opening valve results in super saturation and consequent fog formation in the sampling chamber. Limited size discrimination can be achieved by controlling the partitioning volume in the auxiliary chamber\textsuperscript{45}. According to manufacturer the instrument can count $10^2 - 10^7$ nuclei cm\textsuperscript{-3} with 10% accuracy and suction rate of 10 L min\textsuperscript{-1}.

The hourly vehicular survey has also been conducted from 0600 to 1800 hrs LT once every week on main NH-21 of valley. The hourly vehicles averaged for entire month and year were calculated and compared with particle density.

4 Results and discussions

The hourly measurement for each size mode taken during 2008 including nucleation burst (NB) events, a process of conversion of atmospheric precursor gases into large numbers of ultrafine particles\textsuperscript{14}, has been presented and analyzed.

Figure 3 shows hourly variations of ultrafine particles of various sizes for all 85 measurement days during January–December 2008. In January, weather conditions were rainy and valley witnessed snow everywhere and therefore, readings during 0000-0800 hrs LT could not be taken due to deficiency of manpower. For all other months, readings at every hour have been taken from midnight to midnight. The dd-mm-yy-hr format has been used to plot particle density averaged at every hour of measurement day.

![Schematic diagram of the instrument](image-url)
The hourly variation of particle density for the three sizes were found to be 200 N cm$^{-3}$ (smallest) to 8,00,000 N cm$^{-3}$ (largest), a trend found at various hilly forest sites$^{46-48}$. Also, it is seen that for all three size modes, most of time particle density lies below 50,000 N cm$^{-3}$ except few peaks due to nucleation bursts. The aitken mode (20 nm) density is slightly more than 3 nm nucleation mode which is also slightly more than 1 nm nucleation mode values. The weak nucleation bursts (50,000-70,000 N cm$^{-3}$) are found to be very frequent while moderate (70,000-1,00,000 N cm$^{-3}$) and strong (1,00,000-2,00,00 N cm$^{-3}$) nucleation bursts are few while very strong bursts (>2,00,000 N cm$^{-3}$) are rare.

Figure 4(a) shows frequency of total nucleation bursts for the various months of 2008. It shows gradual rise of occurrence of NB from January attaining maximum in peak summer month of June and then showing fall in occurrence of NB. The frequency is small in winter. The reasons for
maximum NB in summer could be more photochemical reaction in atmosphere due to increased sun’s radiations and also due to increased sulphurous and other organic compounds produced by increased vehicular flow\textsuperscript{49}.

Figure 4(b) shows that out of total 314 NB, there were maximum 196 weak bursts; 75 moderate; 27 strong and 16 very strong NB, while Fig. 4(c) shows that the occurrence of weak and moderate NB were very frequent in summer and gradually decrease in rainy and winter seasons but strong and very strong NB were found mostly in rainy season. The reason for this could be low concentration of pre-existing aerosols due to wash out effect coupled with low temperature during rain leading to triggering of nucleation\textsuperscript{19}. Also, as hilly environment mostly contain hygroscopic primary aerosol particles, hence, increased humidity in rainy season leads to large scale condensation of precursor gases on them producing large scale hydrogenous nucleation\textsuperscript{12}. It is found from Fig. 5(a) that there is almost same frequency of NB of particles of different sizes on monthly basis. The 200 A NB is slightly more than 30 A; and 30 A sized particle’s NB are slightly more than 10 A particles. Out of 314 NB for entire 2008, 122 were found for 200 A; 96 for 30 A; and 96 for 10 A sized particles. The frequency is maximum during forenoon hours and significant during evenings while it is less predominant in early mornings and afternoons as is evident from Fig. 5(b). These results are consistent with those found in earlier studies\textsuperscript{50}.

Figure 6 shows hourly variation of particle density when averaged for all measurement days of month at each particular hour of day for different size range. From Fig. 6, it is found that on monthly basis the particle density gradually rises from January to June/July and then decreases in winter; and hourly variation shows slight jumps during morning and evening traffic hours. Figure 7 shows monthly diurnal traffic flow in valley morning till evening and depicts slight jump in vehicular movement in morning and evening office hours. However, throughout morning till evening, the vehicular flow is following almost the same pattern each hour for all months.

Figure 8 shows good correlation of particle concentration with traffic density along with slight jumps of particle density in morning and evening office hours\textsuperscript{21}. In all the three size range, it has been observed that concentration is slightly high during peak traffic hours, i.e. concentration rises from 0500 hrs LT, reaches peak around 0800 hrs LT then decreases slightly with minimum around 1400-1500 hrs LT and then again starts increasing.

For particles of 200 A size, maximum annual average density is found to be 27350±4246 N cm\textsuperscript{-3} at 0800 hrs LT while minimum density is found to be 10935±2031 N cm\textsuperscript{-3} at 1400 hrs LT while for 30 A and 10 A particle sizes, these maximum values are found to be 24800±3150 N cm\textsuperscript{-3} and 11412±2067 N cm\textsuperscript{-3} at 0800 hrs LT; and minimum at 26345±3471 N cm\textsuperscript{-3} and 11020±1872 N cm\textsuperscript{-3} at 1500 hrs LT, respectively. These results are similar to the trend found in flat hill stations Malampuzha and Sulthan Bathry of Kerala\textsuperscript{51} where annual hourly particle density of particles of size 1-0.01 µm during 2008 was found to be fluctuating in the range 5000 - 15000 particles cm\textsuperscript{-3} for most of the time of the day. At the site under present study, the annual average hourly density for all three sizes were found fluctuating around 18,000 particles cm\textsuperscript{-3} for most of the time of the day and is much higher as comparable to the second site of Kerala. The concentration of ultrafine
Fig. 6 — Monthly average hourly variation of particle density of particle of size: (a) 20 nm; (b) 3 nm; and (c) 1 nm

Fig. 7 — Average hourly numbers of vehicles plying on main NH-21 for various months of 2008

Fig. 8 — Annual average hourly variation of particle density of three sizes for entire 2008
particles during nucleation burst event was reported to fluctuate around 2500 and 5000 particles cm$^{-3}$ at foreign hilly site Tomsk (rural) & Listyanka (semi-rural). The values observed were not only considerably greater than these rural sites rather they are greater than some cities of Europe like Helsinki, Stockholm and Augsburg where annual ultrafine particle density averages around 10,000 particles cm$^{-3}$. The annual hourly variation of vehicle movement when averaged for all months of 2008 is shown in Fig. 9.

Figures 8 and 9 show that the relation of particle density with vehicular traffic is significant. Morning till evening, there is continuous flow of tourist and local traffic and particle density is almost same except faint jumps at traffic rush hours. Further, density of particles of size range 200 A is slightly more than particles of size 30 A; while density of particles of size 10 A is smallest mostly but there are exceptions to this trend mostly during traffic hours when 10 A concentration becomes comparatively more. The rise of particle density in morning rush hours is due to increased vehicular rush and low height of inversion layer. As the day advances, the inversion layer deforms and rises to greater heights till evenings provided day is warm while traffic rush also becomes slightly low by afternoon. Both these factors lower the particle density by afternoons. By the evenings, earth surface starts becoming cold and so the mixing layer drifts downwards slowly. Figure 10 shows plot of 24 h average of particle density for each measurement day of 2008 showing general trend of particulate density on monthly basis in this region. It is found from Fig. 10 that 24 h average of particle density for each measurement day and for each size gradually rises from January, becomes large in June/July. The abnormally large peaks in June, July and August 2008 may be due to super nucleation bursts during these months. There has been 7, 8 and 1 NB of strength 2,00,000-3,00,000 particles cc$^{-1}$, respectively in these months.

The annual variation of 24 h averaged value of particle density of three sizes is depicted in Fig. 11, which shows gradual increase of particle density on annual basis from January to peak tourist summer season of June; and then it gradually decreases in rainy season and becomes small in winter. In plains, during winter season pollutant particles remain lower near earth surface and hence particle density is found more in winter than in summer due to shallow
inversion layer. In mountain valleys due to snow along higher hill surfaces, the temperature is low at hilltops than in valley floor so convection up the valley leads to formation of higher inversion layer along mountain tops and so pollutant particles convect up to mountain tops. The advection of warm layers over valley top layers from far plains can also be the reason of higher inversion layer at this site and another plausible reason can be high frequency of nucleation bursts during summer. Thus, at experimental site, the trend is opposite to plains, i.e. density is higher in summer than in winter. Such a trend has been found in some hilly stations like Puy de Dome, France. The highest monthly 24 h averaged particle density of 200, 30 and 10 A sizes was found to be $25910\pm5819$, $27846\pm5802$ and $21693\pm2595$ N cm$^{-3}$, respectively in June while lowest values of the same were found to be $6861\pm833$, $4791\pm888$ and $3406\pm904$ N cm$^{-3}$, respectively in December. The annual 24 h average for entire 2008 was found to be $18045\pm1212$, $16811\pm2790$ and $15407\pm3109$ N cm$^{-3}$, respectively for particles of 200, 30 and 10 A particle sizes, respectively. A 450% increase of annual particle density for 200 A sized particles was observed as compared to earlier studies conducted in 2000.

This annual variation of particle density is also consistent with annual vehicular movement data as shown in Fig. 12.

The comparison of Figs 11 and 12 shows the same trend of particle density and vehicular movement for different months of 2008. The abnormal rise in September (5125) and October (5187) in vehicular movement is due to month long international fair Dussehra, which started on 6 Oct 2008. The same abnormal rise during these months has been found in particle density also. More value of particle density in rainy season in July can be due to foggy conditions and frequency of large number of NB may also be the reason. In August, comparatively low value can be due to frequent rains and wash/rain out effect and scavenging of fine particles to form cloud condensation nuclei.

The monthly and annual tourist arrival data for 2004-2008, provided by District Tourism Officer (DTO), shown in Fig. 13 reveal that tourists flow is more in summer months and less in winter but gradual buildup of tourist movement has been observed during 2004-2008. The result indicates the impact of tourist as well as local vehicles on the rise of fine particulate matter in the valley.

![Fig. 11 — Annual variation of 24 h averaged value of particle density of each size for 2008](image1)

![Fig. 12 — Annual vehicle movements per day on main national highway-21 in valley for 2008](image2)
5 Conclusions

Based on the analysis of the data, the following conclusions are drawn:

1. The hourly variation of particle density for particles of given size ranges were observed to be varying in the range 200 - 8,00,000 Ncm\(^{-3}\); a trend found at various hilly forest sites\(^{47,48}\).

2. The occurrence of large numbers of particles, called nucleation bursts, was found large in summer and small in winter. The weak and moderate nucleation bursts were found in all seasons while few very strong nucleation bursts were found in June, July and August. Also, more NB’s were found during sunrise/morning and evening traffic rush hours while less during afternoons. For all the particles sizes, almost same numbers of NB’s were observed.

3. The gradual buildup of 24 h averaged value of particle density were found from January onwards and highest in the month of June (the month of maximum tourist flow in the valley). In July, although tourist flow is reduced but foggy conditions of pre-monsoon season may be the reason of large particle density. In August, the wash out effect of rain reduces the particle density. In September and October, month long international festival in valley leads to abnormally increase the particle density.

4. The buildup is more pronounced in summer than in winter, a trend opposite to plains but found in some hilly stations like Puy de Dome, France\(^{57}\) and most plausible reasons can be: high frequency of nucleation bursts\(^{56}\) during summer; higher temperature inversion layer formed along snowy hilltops due to site being on valley floor; and advection of warm layers from adjoining plains during winter.

5. There is good correlation between vehicular flow and ultrafine particle density on annual basis. Also, the tourist inflow data to the area supplements the vehicular flow and particle density data.

The results suggest that nucleation (nanoparticles) and aitken nuclei concentration from petrol/diesel exhaust and many other sources have been considerably increased in this part of Himalayan region.

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