Chemical composition of size-separated aerosols at two rural locations in the Himalayan region

Indian Institute of Tropical Meteorology, Pune 411 008
and
J C Kuniyal
G B Pant Institute of Himalayan Environment and Development, Kullu 175 126

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Size-separated atmospheric aerosols were collected at Kothi (a hill top) and Mohal (a valley), situated at the foothills of western Himalayas during the summer season of 1999. Bimodal distribution of aerosols was observed at both the locations. However, at Kothi, fine size particles dominated (62%), whereas at Mohal, coarse size particles contributed more (75%). The SO4 and NO3 particles together contributed ~ 30% of the total measured chemical composition of aerosols. Burning of biomass and emissions from tourist vehicles could be the main local sources for these components. However, aerosols showed alkaline nature ($\Sigma \Sigma^*$ ratio < 1) due to the neutralizing effect of some cations such as Ca and NH4.

1 Introduction

Aerosols, the tiny entities, play a giant role in some very vital atmospheric phenomena such as radiation balance, cloud microphysics, atmospheric electricity, acid deposition, etc. However, due to the vast range of spatial as well as temporal variations of these particles, it is very difficult to study their characteristics and form the aerosol budget on a global scale. The chemical composition of aerosols is the manifestation of the chemical state of the atmosphere at any place. In fact, the study of the size-separated chemical constituents of aerosols helps in assessing the causes behind acidic/alkaline nature of the aerosols.

In India, studies related to chemical composition of size-separated aerosols have been mostly confined to the urban/industrial regions. However, such studies from remote/least polluted regions are very few. Therefore, observations relating to the mass size distribution of atmospheric aerosols and their chemical components were undertaken at two different locations at the foothills of the western Himalayan region, i.e. at Mohal (31° 54' N, 77° 07' E, 1219 amsl) and Kothi (32° 19' N, 77° 11' E, 2530 amsl) in the Himachal Pradesh state of north India (Fig.1). Apart from being remote locations, these two places are at different altitudes and the adjoining topography is also not the same. Thus, these observations would also provide the opportunity to study the spatial variation of aerosols and their chemical constituents in this region.

Himalayan region has its own unique character. It is rich in biodiversity concerning both flora and fauna. It is a source of major rivers like Ganga, Yamuna, Bias, etc. It plays a central role in regional scale atmospheric circulation over Asia and is very vital for mechanism of summer monsoon. Recently, in the past few years, due to the increasing human intervention (especially, due to tourism, urbanization, deforestation and biomass burning), the natural ecosystem of this region has been threatened with the perturbation of long established biogeochemical cycles. For any assessment of the changes in the atmospheric composition of this region, it is essential to monitor the major atmospheric constituents. Studies related to chemical composition of aerosols in the Himalayan region are very few. The present study is an attempt in this direction.

2 Site descriptions

Observations were carried out at Mohal near Kullu during 19 May-26 May 1999 and at Kothi near Manali during 27 May-1 June 1999. The sampling site at Mohal was located in the campus of G B Pant Institute of Himalayan Environment and Development. Mohal is a rural location situated in the Kullu valley that comprises Himalayan Beas basin of the valley. The sampling site is about 700 m away from the nearby
Fig. 1—Locations of the sampling sites

national highway. It is about 5 km to the south of the Kullu town. Sampling was conducted at a height of about 3 m from the ground. Apples and apricots are the major plantations in the nearby surroundings. The sampling site at Kothi was near the government guest house, situated on the hilltop. It is on the way from Manali to Rohtang Pass. Observations at Kothi could serve as representative of background concentrations for this region, as there is very little human interference.

3 Methods of sampling and analysis

Sampling of size-separated aerosols was carried out using a Low Volume Air Sampler (Andersen, 2000; Andersen Inc., USA make) which collects particles on 9 different stages with sizes ranging from < 0.08 \( \mu m \) to 9 \( \mu m \) rad. Whatman 11 filter papers of 8 cm dia. were used for the collection of aerosols. Particles were collected at the flow rate of about 28 lit min\(^{-1}\). The net aerosol load on the filter papers was determined by weighing the filter papers before and after sampling with a microbalance in humidity-equilibrated environment. The filter papers were then extracted for the chemical analysis of water and acid-soluble components of aerosols. Metallic components, i.e. Na, K, Ca and Mg, were analysed using atomic absorption spectrophotometer. Whereas, colorimetric methods were used for the analysis of NH\(_3\), Cl and SO\(_2\). Details of sampling and analysis have been mentioned elsewhere.

4 Results and discussion

4.1 Aerosol size distributions at Mohal and Kothi

Figure 2 shows the mass size distributions of aerosols and their chemical components at Kothi and Mohal. Aerosols showed bimodal size distributions at both the places with a peak in fine (0.43 \( \mu m \)) and coarse (4.7 \( \mu m \)) size each. This indicates the contribution from both the primary and the secondary particles. Figure 3 shows the percentage contributions of fine and coarse size particles for aerosols and their chemical components at both Kothi and Mohal. Mass median diameters (MMD) are shown in Table 1. Coarse size particles contributed more (75\%) at Mohal, whereas, at Kothi, fine size particles contributed more (62\%) to the total aerosol load. The MMD values also showed dominance of fine size particles (1.22 \( \mu m \)) at Kothi and that of coarse size particles (5.23 \( \mu m \)) at Mohal. The high altitude of Kothi could be the major reason for less contribution of coarse size particles. Whereas at Mohal, soil-oriented coarse particles were dominant due to more human activities such as constructions, agriculture, etc.

Most of the studies conducted on mass size distribution of aerosols at different locations in India, have reported a bimodal distribution with a peak, each in fine and coarse size ranges. However, coarse size has generally dominated, indicating the major contribution from natural sources such as sea and soil. However, at Silent Valley, a dense forest region in south India, fine size particles have been reported to dominate over the coarse size, which was attributed to certain biogenic sources such as vegetational emissions as well as due to the absence of open.
Fig. 2 — Mass size distributions of aerosols and their chemical components at Kothi (- + -) and Mohal (- o -)

Fig. 3 — Percentage contributions of fine and coarse size particles to total aerosols and their chemical components at Kothi and Mohal
land/loose soil in the surroundings. A bimodal distribution of aerosols is reported at Mohal, Kullu, during studies conducted in the summer seasons of 1996 and 1998, with coarse size contributing more (~60%) than the fine size. Bimodal distribution of aerosols has also been observed at Kosi, about 11 km from Almora, U P, situated at the foothills of the western Himalayan region, at about 1100 m asl. Mass size distribution of aerosols at Kosi during both pre-monsoon (May 1994) and post-monsoon (October 1993) seasons showed the dominance of coarse size particles (~ 60 - 70% of total aerosols) over the fine size.

Thus, it seems that in the north Indian region, coarse size particles dominate over the fine ones, even at the height of about 1000 m asl. This could be attributed to high convective activity in this region, especially during summer months, that raises the particles of local land origin and also due to the transport of air masses from the adjoining arid zones of Rajasthan due to westerly winds. Contribution from fine size particles increases as we go to still higher (> 2000 m asl) locations like Kothi.

As seen from Fig. 3, concentrations of aerosol as well as its chemical constituents were more in the fine size than in the coarse size at Kothi as compared to those at Mohal, except NH₃. Similarly, the MMD values as shown in Table 1, were more (except NH₃) at Mohal than those at Kothi. Due to its high altitude and also due to comparatively more vegetation in nearby surroundings, fine size particles showed more contribution towards total aerosol as well as its chemical constituents at Kothi.

4.2 Crustal components

Particles originating from crustal source are generally in the coarse size. At Mohal, apart from Ca (74%), Mg (71%), and K (53%), NO₃ also showed more contribution in coarse size. Also, the MMD values were quite high for Ca (4.81 μm), Mg (2.62 μm) and K (2.62 μm). Whereas, at Kothi, Ca (57%), Mg (54%) and NH₄ (52%) showed more contribution in coarse size with their MMD values being 3.30 μm, 2.71 μm and 2.20 μm, respectively. This indicates that contribution from the crustal source was significant, especially for Ca and Mg at both Mohal and Kothi, whereas it contributed significantly for K at Mohal. Both the fine and coarse size particles contributed equally for NO₃ at Mohal as well as at Kothi. Coarse size NO₃ aerosols could be attributed to the adsorption of HNO₃ vapours on coarse size soil-oriented particles such as Ca, Mg or K.

Considering Ca as the reference element for crustal sources, enrichment factors were calculated for K, Mg and SO₄-S. Table 2 gives these enrichment factors. The crustal composition has been taken from Horn and Adams. It was observed that while K and Mg showed non-enrichment, SO₄-S showed very high enrichment at both Mohal and Kothi. This indicates soil as a major source for K and Mg.

4.3 Marine components

Generally, sea is considered to be a major source for Cl, Na, Mg and, to some extent, for SO₄-S. However, sea-salt aerosols, like crustal ones are in the coarse size. At Mohal as well as at Kothi, Cl showed equal contribution in coarse and fine sizes, whereas coarse size was dominant in case of Na and Mg.

Considering Na as the reference element for marine source, enrichment factors were calculated for Cl, K, Mg and SO₄-S and are given in Table 3. Marine composition has been taken from Goldberg et al. As seen from Table 3, Cl showed non-enrichment at both Mohal and Kothi, indicating dominance of marine source. But K, Mg and SO₄-S showed high enrichments indicating very little contribution from sea water. Similarly, non-sea-salt (nss) fractions for K, Mg and SO₄ were calculated, considering Na as a

<table>
<thead>
<tr>
<th>Location</th>
<th>K</th>
<th>Mg</th>
<th>SO₄-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mohal</td>
<td>0.54</td>
<td>0.56</td>
<td>12.9</td>
</tr>
<tr>
<td>Kothi</td>
<td>0.20</td>
<td>0.42</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 1 — Mass median diameters (μm) for TSP* and its chemical constituents at Kothi and Mohal

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass median diameter (μm) of components at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kothi</td>
</tr>
<tr>
<td>TSP</td>
<td>1.22</td>
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<tr>
<td>Cl</td>
<td>1.87</td>
</tr>
<tr>
<td>Na</td>
<td>1.99</td>
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<tr>
<td>Mg</td>
<td>2.71</td>
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<tr>
<td>K</td>
<td>1.10</td>
</tr>
<tr>
<td>Ca</td>
<td>3.30</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.60</td>
</tr>
<tr>
<td>NO₃</td>
<td>2.10</td>
</tr>
<tr>
<td>NH₄</td>
<td>2.20</td>
</tr>
</tbody>
</table>

* Total suspended particulates

Table 2 — Enrichment factors for the crustal source (Ca as reference element) for aerosols at Mohal and Kothi
reference element. Here, K showed almost 98-99% contribution from sources other than sea. Also, for Mg, about 20% contribution came from marine source, while rest of it could be attributed to the crustal source. The SO$_2$ showed ~94% contribution from non-marine sources at Mohal, whereas at Kothi, it was ~80%.

4.4 Anthropogenic components

Apart from the industrial and vehicular emissions, changing agricultural practices and biomass burning are the other major sources for the compounds of sulphur and nitrogen, heavy metals and a wide range of organic compounds. However, at places like Mohal and Kothi, in spite of the absence of any major industrial activity, the concentrations of SO$_4$ and NO$_3$ were significant which could be attributed to either emissions from vehicles running on the nearby roads (being the tourist places, the traffic densities were quite appreciable on these roads, especially, during morning and late afternoon hours; approximately ~2.6 lakh tourists visit Kullu every year) or due to burning of wood or cow dung in local surroundings for cooking and/or agricultural purposes.

Natural sources did not contribute significantly for SO$_2$ (as seen from the crustal and marine enrichment factors). The SO$_2$ was mainly in the fine size (80% at Mohal and 96% at Kothi, with MMDs < 1 µm). However, as seen from Fig. 4, the molecular form of SO$_2$ was different at Kothi than that at Mohal. The respective contributions from fine (80-85%) and coarse (15-20%) size particles were almost equal for both NH$_4$ and SO$_4$ at Mohal and also their MMD values were equal (0.89 µm for both). This suggests that at Mohal, SO$_2$ could be in the form of ammonium sulphate, which is not an acidic form of SO$_2$. Whereas, at Kothi, not only the contribution from fine and coarse size particles but the MMD values were also different for both SO$_4$ and NH$_4$. In fact, SO$_2$ did not show a significant relation with any other measured constituent of the aerosol. Therefore, it could be in the form of H$_2$SO$_4$ which has an acidic potential. This acidic potential is reflected in rain water pH at Kothi, where about 43% of the samples were found to be acidic. It is reported that ozone plays an important role in the acidification, as it enhances the oxidation of SO$_2$ to SO$_4$ (Refs 22, 23). The average concentration of O$_3$ was ~40 ppb at Kothi, whereas at Mohal was ~20 ppb (Ref. 24). This could be one of the reasons for the formation of H$_2$SO$_4$ in aerosols at Kothi.

At Kothi, NH$_4$ could be in the form of NH$_4$NO$_3$ as the percentage contributions of fine and coarse size particles for both NH$_4$ and NO$_3$ were almost equal (~50 each) and, in addition to it, their MMD values (~2.2 µm) were also nearly equal. This can be better seen from the cumulative size distribution plots drawn for particle diameter (D$_p$) against cumulative percentage in each size range for NH$_4$, NO$_3$, and SO$_4$ (Fig. 4). It can be seen from these plots that they were similar for NH$_4$ and NO$_3$ at Mohal, whereas at Kothi, NH$_4$ plot was similar to the plot of NO$_3$ and did not resemble that of SO$_4$. The low temperature (average 14°C with a variation of -2°C to 22°C during the observational period) and low relative humidity (~45%) at Kothi provided conducive atmosphere for the formation of NH$_4$NO$_3$ (Refs 25, 26).

Coarse NH$_4$ observed at Kothi (about 50% contribution in coarse size) was in the form of ammonium nitrate. Zhuang et al. have reported the presence of coarse ammonium aerosols and have suggested that it was possibly formed by the reaction of NH$_3$ on sulphate or nitrate-enriched sea-salt and soil particles, if excess ammonia gas was available. At Kothi, the presence of excess NH$_3$ gas, mainly due to the local activities like cattle grazing and biomass burning, could have led to the reaction of this excess NH$_3$ with nitrate-enriched soil particles. Ammonium showed identical size distribution like nitrate with the coarse size peak at 3.3 µm (Fig. 2) and also, as stated earlier, their MMD values were nearly equal. Similar justification has been reported for the presence of coarse NH$_3$ with its peak in the same particle size as that of NO$_3$ (Ref. 28). In fact, concentration of NH$_4$ was also more in rain water at Kothi and its

<table>
<thead>
<tr>
<th>Location</th>
<th>Cl</th>
<th>K</th>
<th>Mg</th>
<th>SO$_4$-S</th>
<th>Non-sea-salt SO$_4$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mohal</td>
<td>0.9</td>
<td>24.0</td>
<td>4.8</td>
<td>19.0</td>
<td>94</td>
</tr>
<tr>
<td>Kothi</td>
<td>0.5</td>
<td>13.0</td>
<td>5.1</td>
<td>4.9</td>
<td>80</td>
</tr>
</tbody>
</table>
neutralizing capacity was more as compared to that of Ca.

4.5 Acidic potential of aerosols

Among the anions, SO$_4$ concentrations were slightly more than those of NO$_3$ at Mohal (SO$_4$/NO$_3$ ratio was 1.08), whereas, at Kothi, NO$_3$ concentrations were about one order more than SO$_4$ concentrations (SO$_4$/NO$_3$ ratio was 0.12). The ionic ratios ($\Sigma^-/\Sigma^+$) at both Mohal and Kothi were < 1 which indicate towards alkaline nature of aerosols. The percentage contributions of different ionic components of aerosols (in both fine and coarse size fractions) at Mohal and Kothi are shown in Figs 5 and 6, respectively. It can be seen from these figures that the contributions of SO$_4$ and NO$_3$ were < 30 % at both the places, whereas those of Ca and NH$_4$ were ~ 50 %. Also, the sea-salt constituents (Na and Cl) contributed < 15 %. Thus, the acidic potential of aerosols was counter-balanced by cations like Ca, NH$_4$, Na, K and Mg. The total concentration of SO$_4$ was itself very less at Kothi (~ 8 n eq m$^{-3}$) as compared to that at Mohal (~ 45 n eq m$^{-3}$). Therefore, eventhough fine size particles contributed more for SO$_4$ (about 96 %), and that it could be in the form of
Fig. 6 — Percentage contributions of different ionic components of aerosols at Kothi

H\textsubscript{2}SO\textsubscript{4} still the aerosols showed alkaline nature. Also, NO\textsubscript{3} concentration was more at Kothi, but it was in the non-acidic coarse size, formed through reaction with either crustal (Ca, K, Mg) or Marine (Na) components. In addition to it, fine size NO\textsubscript{3} at Kothi was in the form of NH\textsubscript{4}NO\textsubscript{3} and not HNO\textsubscript{3} resulting in non-acidic nature of aerosols.

Even though, the chemical nature of aerosols at Kothi and Mohal was alkaline, the concentrations of acidic ions, i.e. SO\textsubscript{4} and NO\textsubscript{3} were considerably more which is mainly attributed to the local sources, such as biomass burning for household purposes. Also, vehicular emissions due to tourist activities are contributing to the emissions of precursor gases of acid aerosols. Transport of pollutants to this region from other places seems to be a distant possibility as there are no major industries in the surroundings of the sampling sites. However, further studies on trajectory analysis could throw some light on the role of long range transport of pollutants to this region from north Indian industrial areas of Delhi, west Uttar Pradesh and Punjab, which lie to the south-west of the Kullu valley, especially, when the winds are from south-west in the monsoon season.

5 Conclusions
The study conducted on mass size distribution of aerosols and their chemical components at Mohal and Kothi in the Himalayan region indicates that despite the absence of major industrial activity, the concentrations of the acidifying constituents such as SO\textsubscript{4} and NO\textsubscript{3} were substantial. This could be mainly due to the local sources such as biomass burning in the surrounding areas and also partly due to the emissions from tourist vehicles. However, the chemical nature of aerosols was alkaline due to the neutralizing effect of cations such as Ca, K, Mg and NH\textsubscript{4}. The NO\textsubscript{3} showed considerable contribution (50 \%) in course size, which was in the form of NH\textsubscript{4}NO\textsubscript{3}. The SO\textsubscript{4} was in the form of ammonium sulphate at Mohal, which is non-acidic. Whereas, at Kothi, it was in the form of H\textsubscript{2}SO\textsubscript{4}. However, concentration of SO\textsubscript{4} in aerosols was less at Kothi as compared to that at Mohal. The results obtained in this study, especially those at Kothi, could be used as background values for this region for future studies on aerosol composition.

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