Water Soluble Ionic Components in Particulate Matter (PM₁₀) during High Pollution Episode Days at Mohal and Kothi in the North-Western Himalaya, India

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ABSTRACT

Particulate pollutants and their water soluble ionic components were collected and analyzed on the occasion of high pollution episode days in the period 2009 to 2011. Among the water soluble ionic constituents at Mohal (valley base), SO_4^{2-} (34%) was the largest contributor; followed by Cl^- (20%), NO_3^- (17%), Ca^{2+} (9%), Na^+ (7%), NH_4^+ (5%), F^- (2%), Zn^{2+} (2%) and Mg^{2+} (1%). While at Kothi (hill slope), Cl^- (27%) was the largest contributor; followed by SO_4^{2-} (25%), NO_3^- (14%), Na^+ (11%), Ca^{2+} (9%), NH_4^+ (7%), K^+ (3%), F^- (3%) and Zn^{2+} (1%). The average ratios of $NO_3^- + Cl^-/SO_4^{2-}$ were 1.08 and 1.64 for Mohal and Kothi, respectively; indicating that a small fraction of HNO_3 and HCl influenced the acidic nature of ions. The mass ratios of NH_4^+/NO_3^- and NH_4^+/SO_4^{2-} were 0.29, 0.5 and 0.15, 0.28; at Mohal and Kothi, respectively. The ratios were below unity showing the predominance of NH_4NO_3 and $(NH_4)_2SO_4$ in the atmosphere. The descending order of neutralizing factors were observed as $Ca^{2+} > NH_4^+ > K^+ > Mg^{2+}$ assuming that the origin is of a crustal source. The non-sea salt fraction for Mohal was found in the descending order of Cl^-, Ca^{2+} and SO_4^{2-}, which are more than 50% of the total ions except Mg^{2+} and K^+. While for Kothi, the percentage of Cl^- and SO_4^{2-} stood to be more than 50% indicating that these ions are of non-marine origin. The first factor from principal component analysis for Mohal explains 75.59% of the total variance i.e., highly loaded with NH_4^+ (0.986), K^+ (0.685), F^- (0.935), Cl^- (0.919) and Zn^{2+} (0.969) indicating influence of anthropogenic activities on PM_{10} concentration. While at Kothi, the first factor explains 45.41% of the total variance, highly loaded with K^+ (0.981), SO_4^{2-} (0.965), NO_3^- (0.953) and Zn^{2+} (0.948) also indicating influence of anthropogenic activities in the region.

Keywords: Particulate pollutants; Ionic species; Neutralization factor; Anthropogenic activities; Factor analysis.

INTRODUCTION

Aerosols have dynamic links between their sources, transport vectors and deposition sites; and these linkages vary according to different pollutants in the atmosphere (Safai *et al.*, 2005). The acidic and alkaline nature of aerosols can be assessed by studying the chemical constituency of aerosols (Safai *et al.*, 2010). The quantity of aerosols has been increasing as a function of human and anthropogenic activities; consequently imparting an increasing impact upon climate change (IPCC, 2001, 2007). It is therefore important to study the physical and chemical properties of aerosols to understand their transformation processes, as occurring in the atmosphere. The aerosols have their direct (scattering and absorption of incoming solar radiation) and

indirect effects (facilitates formation of clouds by acting as condensation nuclei) depending upon their size distribution and chemical composition (Tiwari *et al.*, 2010). The composition of an aerosol is particularly dependent on its granulometric size, such as in the case of: SO_4^{2-}, NH_4^+, organic compounds and some transition metals which remain present in the fine fraction ($PM_{2.5}$). In contrast, crustal material such as: Si^{4+}, Ca^{2+}, Mg^{2+}, Al^{2+}, Fe^{2+} and some biogenic compounds like pollen, spores and vegetable debris are generally found in the coarse fraction i.e., PM_{10}–$PM_{2.5}$ (Avino *et al.*, 2006). Nitrite and sulphate aerosols are, however, produced as a result of the interaction among ammonia, NO_x, SO_2 and other gaseous constituents (Manigrasso *et al.*, 2010).

Aerosols dominated by sulphate reflect the solar energy (Moorthy *et al.*, 1998; Sathees *et al.*, 2001), whilst aerosols dominated with black carbon absorb heat. The sulphate aerosols cause a cooling effect near the Earth's surface, while black carbon aerosols cause a heating effect in the atmosphere. The scattering and absorption from incoming solar radiation can bring about a change in the radiation

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budget of the Earth's atmosphere, leading to climate change (IPCC, 2007). In India, aerosols are generally reported to be of an alkaline nature with neutralization of acidity mainly due to the cations like Ca^{2+} and NH_4^+ (Khemani, 1994; Safai *et al.*, 2005; Kumar *et al.*, 2002). The natural sources of aerosols like mineral aerosols (soil) and sea salt aerosols (sea) have been found to affect their concentration and composition. The marine aerosols dominate over coastal regions, while aerosols of a crustal and anthropogenic origin dominate over continental interiors (inland locations) (Kulshrestha *et al.*, 2010). In coastal areas, the natural aerosol source is sea salt which is considered to be harmless from a health point of view, and has an important contribution in increasing PM level. It is with this rationale that some governments have implemented derogation guidelines for sea salt (Manders *et al.*, 2009). It has also been observed that with increasing industrial development and urbanization, the contribution from anthropogenic sources has increased notably in the urban and industrial locations (Praveen, 2008). Further, massive biomass burning during winter months also plays a role in the loading of anthropogenic aerosols over Darjeeling (Chatterjee *et al.*, 2010) as well as Kullu-Manali, the high altitude regions from the north-eastern to north-western Himalaya, respectively. It can therefore be argued, that the landscape and atmospheric environment in the Himalayas is largely affected by the anthropogenic activities associated with rapid urbanization and development (Kuniyal *et al.*, 2004).

Due to increasing emissions of pollutants associated with fast growing economies in south-east Asia, there has been a progressive increase in aerosol concentrations above those of natural background levels (Gautam *et al.*, 2009a). Observations from satellite data show that the light absorbing aerosols cause haze (which is about 3–5 mm thick) over India, intensifying over the Thar desert and the Indo-Gangetic plain. The Indo-Gangetic plain has a sharp boundary towards the north (i.e., the Himalayas), and to the south extends towards the north Indian oceans (Ramanathan *et al.*, 2007; Gautam *et al.*, 2009b). Ascending Himalayan slopes, valley winds can transport the aerosol rich layer to even higher altitudes (Gautam *et al.*, 2009b). Importantly, these elevated locations coincide with glaciated terrain; indeed most of the glaciers in the Himalayan region have been retreating since 1850 with increasing melting rates due to the transport of optically active aerosols (Mayewski and Jeschke, 1979).

The aim of the present study is therefore to identify the contribution of aerosol loadings at two semi-rural lower and higher altitude settlements (locally termed stations) in the Kullu valley of the north-western Himalaya. This study provides the scientific basis to further investigate atmospheric pollution over the topographically dynamic and ecologically sensitive Himalayan region.

SITE DESCRIPTION

Mohal and Kothi are two experimental sites in the Kullu Valley, Himachal Pradesh, north-western Indian Himalaya (Fig. 1). The G.B. Pant Institute of Himalayan Environment and Development (GBPIHED), Himachal Unit, Mohal, is the lower altitude valley base site (1154 m ASL; 31°54′N latitude, 77°07′E longitude). The higher altitude, steeper gradient site is Kothi (2474 m ASL; 32°19′N latitude, 77°11′E longitude). Kothi is the last inhabited village of the Kullu valley, enroute to the Rohtang Pass (3978 m), which along with Gulaba and Marhi locations, are tourist/recreational hotpots for visitors to Manali.

The lower altitude experimental site at Mohal in the Kullu valley is located in the Lesser Himalayan region, situated 5 km south of Kullu town and 47 km south of Manali town. The Kullu-Manali area, is amongst the more well-known tourist circuits in Himachal Pradesh, standing only second to the Solan-Shimla circuit further south in the State. Urbanization is slowly ongoing at Mohal and therefore this site may be classified as semi-urban. In contrast, Kothi has semi-rural land use characteristics, such as terrace crop farming, alongside seasonal tourism activities (snow sports, sightseeing, and to benefit from the cooler mountain climate and seek an improved health condition).

The present experimental sites provide important ongoing contributions to an understanding of aerosol conditions in the north-western Himalaya. In recent years, the aerosol research has been reported in this region (Momin *et al.*, 2000; Momin *et al.*, 2002; Safai *et al.*, 2002; Kuniyal *et al.*, 2003; Gajananda *et al.*, 2005; Kuniyal and Bhomick, 2005a, b; Kuniyal and Vishvakarma, 2006); consequently it is now developing a reputation in the field of aerosol science (Kuniyal *et al.*, 2005).

METHOD OF SAMPLING AND ANALYSIS

The respirable dust sampler (RDS-460 Envirotech make, CSIR-NEERI improved Technology, India) was used to collect Particulate Matter below 10 μ diameter. The air is drawn through a size-selective inlet and through a 20.3 × 25.4 cm (8 × 10 inches) Whatman filter paper having a flow rate between 1–1.5 L/min. Particles with aerodynamic diameters less than the cut-off point of the inlet are then collected on the filter paper. The total mass of these trapped particles is determined by the difference in filter paper mass prior to and after sampling. The concentration of PM_{10} in the designated size range is calculated by dividing the mass gain of the filter by the volume of air sampled. The collection duration for each sample was about 8 h. The filter paper exposed for PM_{10} samples with highest concentration on daily (pollution episodes), seasonal basis (high to low concentration in descending order) and the local Dusshera festival at Kullu during October (high to low concentration in descending order) were analysed. The single day comprises of three filter papers representing eight hourly sampling.

In the present study, the filter papers containing particulate matter below 10 μm (PM_{10}) were analysed for water soluble chemical components with the help of an Ion Chromatograph (Dionex-3000, U.S.A.). This was based on a 25% of exposed filter paper area sub-sample, with one-fourth analysis to identify the cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+), anions (F^-, Cl^-, NO_3^-, SO_4^{2-}) and transition metals (Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}). Herein, particulates were extracted
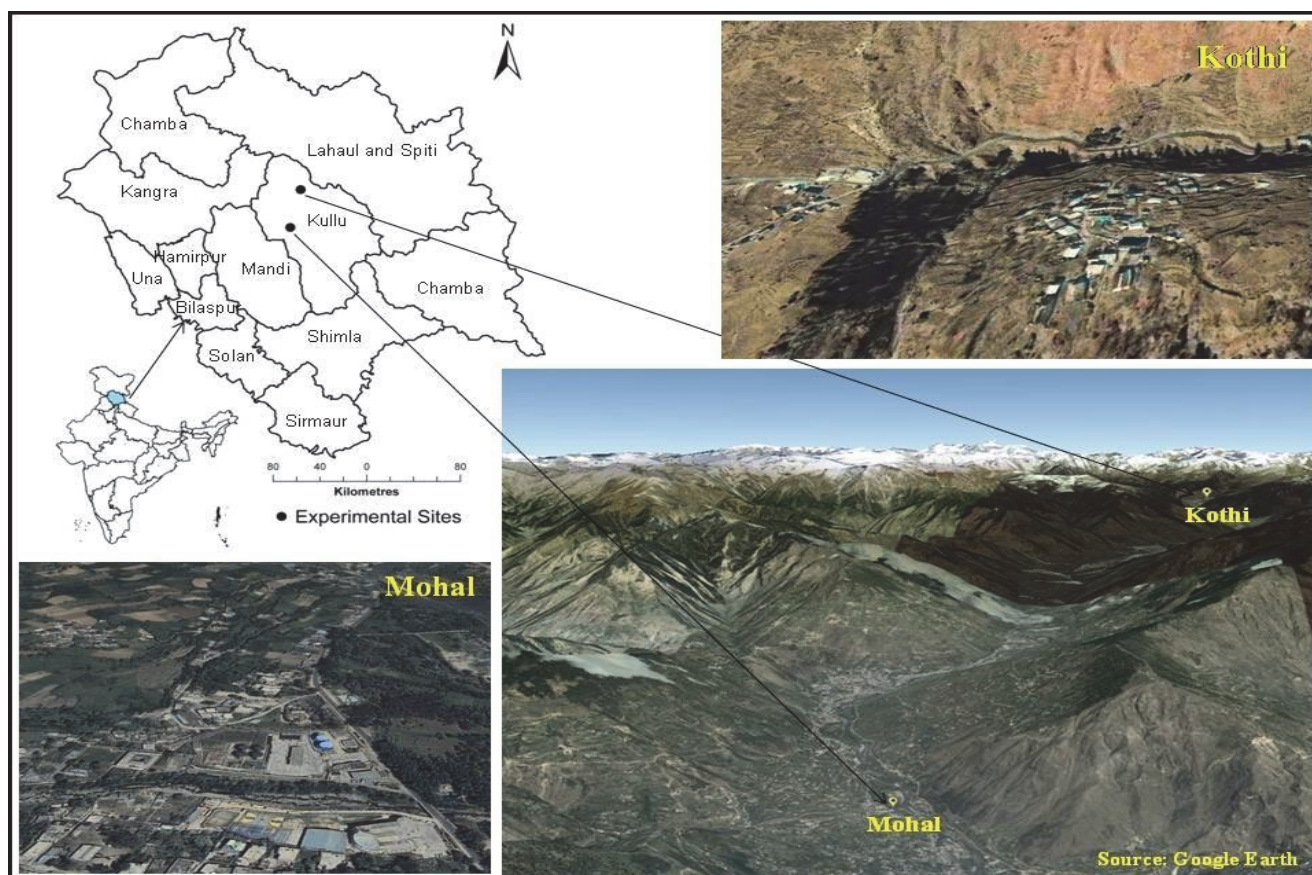
Fig. 1. Geographical location of the experimental sites at Mohal and Kothi.

with ultrapure water (50 mL) via ultra-sonication for 50 minutes. These samples were then filtered through 0.22 μm millipore filter papers into pre-cleaned polypropylene bottles. All filtered samples were preserved in a refrigerator at 4°C. For anions, analytical column AS-11HC (4 × 250 mm), guard column AG-11HC (4 × 250 mm) and suppressor ASRS (300–4 mm) were used with 30 mM NaOH as an eluent having detection limit in parts per billion (PPB). While for cations analytical column SCS-1 (4 × 250 mm), guard column SCG-1 (4 × 250 mm) with non-suppressed conductivity, 3 mM Methane Sulphonic Acid as eluent having detection limit in parts per million (PPM) and triple distilled water were used as a regenerator. The transition metals were also detected by using analytical column CS-5A (4 × 250 mm), guard column CG-5A with Pyridine Di Carboxylic Acid (PDCA) and 4-(2-pyridylazo) resorcinol (PAR) as an eluent. The standards for calibration for cations, anions and transition metals were procured from Dionex (2008).

In order to ensure the accuracy of results, replicate samples were analyzed at every 10th of injection. The limits of detection for anions like F^-, Cl^-, NO_3^-, SO_4^{2-}, Br^-, NO_2^- and PO_4^{2-} were 0.01, 0.02, 0.06, 0.08, 0.06, 0.12 and 0.3 ppm with a 1.5 mL/min eluent flow rate. While the detection limit for cations like NH_4^+, Na^+, Mg^{2+}, K^+ and Ca^{2+} were 0.03, 0.03, 0.08, 0.10 and 0.17 ppm with a 1.0 ml min^{-1} eluent flow respectively. In the case of transition metals, the detection limits of Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} were 0.030, 0.005, 0.013, 0.005, 0.010, 0.013 ppm (mg/L) respectively having a PDCA flow rate of 1.0 mL/min and a PAR flow rate of 0.7 mL/min = 40 PSI ± 0.1 mL/min.

The blank samples were chemically analyzed by using their respective levels of detection limits of samples in the Ion Chromatography system to obtain the final data value. The analytical precision was maintained through running known standard solutions of ionic radicals. Relative standard deviation was used for determining precision which stood to be below 2% of the total different measured ions at experimental sites.

The glasswares used in the analysis of water soluble ions were dipped overnight in a diluted nitric acid, and subsequently washed a minimum of three times with double distilled water to remove any impurities.

For calculating the Neutralization Factor (NF) value of cations, only non-sea salt (nss) fractions of these components were calculated as shown by Eqs. (1)–(4):

$$\left[NF_{NH_4} \right] = \frac{[NH_4^+]}{[NO_3^-] + [nssSO_4^{2-}]} \tag{1}$$

$$\left[NF_{Ca} \right] = \frac{[nssCa^{2+}]}{[NO_3^-] + [nssSO_4^{2-}]} \tag{2}$$

$$\left[NF_{Mg} \right] = \frac{[nssMg^{2+}]}{[NO_3^-] + [nssSO_4^{2-}]} \qquad (3)$$

$$\left[NF_K \right] = \frac{[nssK^+]}{[NO_3^-] + [nssSO_4^{2-}]} \qquad (4)$$

To verify the overall effect of neutralizing components with respect to acidic components, the Neutralization Potential (NP) to the Acidic Potential (AP) was calculated as shown by Eq. (5),

$$NP = Nss\ Ca^{2+} + Nss\ K^+ + Nss\ Mg^{2+} + Nss\ NH_4^+ \qquad (5)$$
$$AP = Nss\ SO_4^{2-} + Nss\ NO_3^-$$

It is observed that some of the cations like Ca^{2+} and Mg^{2+}, and anions like SO_4^{2-} measured over land originate from both the sea in the form of natural salt and from anthropogenic activity. These ions do not play any role in determining the acidity/alkalinity of the aerosols. This is also taken account of while determining the NF value of cations, where only non-sea salt fractions of these components are considered. Assuming that most of the sodium amount is of marine origin, the sea salt fractions were estimated to exclude its fractions in ionic species in the samples (Keene *et al.*, 1986) as is shown by Eq. (6),

$$F_{nss} = \frac{[\chi_c] - [Na^+]\gamma}{[\chi_c]} \qquad (6)$$

where, F_{nss} is the non-sea salt fraction, χ_c denotes concentrations of desired cation and γ is the ratio $[\chi_c/Na^+]$ in sea water.

The factor analysis is a statistical technique (Harman, 1960) which is used for data reduction and to arrange data sets more precisely under present aerosol studies. The technique was used to infer the inter-relationship among the measured ionic species over the experimental sites. Factor analysis was performed for PM_{10} samples (three samples per day) with the help of SPSS (version 16) by utilizing the Principal Component method with Eigen value ≥ 1 (as a cut-off).

RESULTS AND DISCUSSIONS

Concentration of Water Soluble Ions at Mohal and Kothi

The concentration of water soluble ions at Mohal and Kothi include the days with pollution episodes, higher to lower concentrations during different seasons and during the Dusshera festival at Kullu (Table 1). The criteria for analyzing filter papers of particulate matter out of the total exposed samples in every alternate day in a year were kept in a descending order.

The average, maximum, minimum and percentage concentration of water soluble ions is shown in Table 2. The concentrations of ions at Mohal were found from highest to lowest in an order of: $Ca^{2+} > Na^+ > NH_4^+ > K^+ > Zn^{2+} > Mg^{2+}$ among cations; and $SO_4^{2-} > Cl^- > NO_3^- > F^-$ among anions. While at Kothi, the descending order was found to

be: $Na^+ > Ca^{2+} > NH_4^+ > K^+ > Zn^{2+} > Mg^{2+}$ for cations; and $Cl^- > SO_4^{2-} > NO_3^- > F^-$ for anions. It shows at both the sites that cations with the maximum concentrations were calcium, sodium and ammonium, while predominant anionic species were sulphate, chloride and nitrate.

Ionic Ratio of Water Soluble Ions in PM_{10} Exposed Samples

The water soluble PM_{10} ionic concentration for Mohal and Kothi is shown in Fig. 2. Among the ionic constituents at Mohal, sulphate contributed the most (34%) followed by chloride (20%), nitrate (17%), calcium (9%), sodium (7%), ammonium (5%), fluoride (2%), zinc (2%) and magnesium (1%). For Kothi, chloride contributed the most (27%) followed by sulphate (25%), nitrate (14%), sodium (11%), calcium (9%), ammonium (7%), potassium (3%), fluoride (3%) and zinc (1%). While the remaining ions at both the experimental sites were unidentified which is the limitation of the equipment.

The acidic nature is due to sulphuric and nitric acids, and neutralization by cations such as $Ca^{2+} + Mg^{2+}$. The equivalent ratio measured among ionic species have been calculated in order to understand the relative contribution of nitric acid to the total acidic formation in the study area (Table 3). The average mass ratio of NO_3^-/SO_4^{2-} was observed to be 0.5 and 0.56 for Mohal and Kothi, respectively. This shows the influence of sulphuric acid indicating the contribution of acidity in the atmosphere. However, the ratio of such acids more than unity means free acidity which may be due to both- nitric and hydrochloric acid (Khemani *et al.*, 1994). The ratio of $Ca^{2+} + NH_4^+/NO_3^- + SO_4^{2-}$ less than 1.00 indicates that the acidity due to SO_4^{2-} and NO_3^- is not fully neutralized by Ca^{2+} and NH_4^+. This ratio is less than one which means that acidity is more influenced by the sulphate ion (Balachandran and Khilare, 2001).

The mass ratio of NH_4^+/NO_3^- and NH_4^+/SO_4^{2-} was observed as 0.29 and 0.5 at Mohal and 0.15 and 0.28 at Kothi, respectively. These results show that if this ratio is below unity, some compounds may predominate in the atmosphere and remain in the form of NH_4NO_3 and $(NH_4)_2SO_4$ (Seinfeld, 1986). This is also the case at the two sites in the Kullu valley. Moreover, the ammonium nitrate dominates over ammonium sulphate compound (Parmar *et al.*, 2000) in this study. Specifically, it is estimated that the percentage of sulphuric acid ranged from 60% to 70% of the total sample and nitric acid from 30% to 40% of the total sample in PM_{10} filters (Al-Momani *et al.*, 1995; Tunner *et al.*, 2001). The percentage for sulphate and nitrate of the total ions was 66% and 33% at Mohal and 64% and 35% at Kothi respectively indicating larger concentrations of sulphate ion at both the experimental locations. This high level of sulphate may possibly reflect fossil fuel combustion in the immediate region. Additional more distant sources from the Indo-Gangetic/Punjab Plain include: domestic burning of dry dung cakes, preparation of brick kilns by coal fired energy and electricity generation by coal fired power stations.

Neutralization of Aerosol Acidity

The acidic nature of aerosols is mainly due to the

Table 1. PM_{10} samples (mean concentration in $\mu g/m^3$) analyzed for water soluble ionic components during pollution episode days at different occasions at Mohal and Kothi during 2009–2011.

Mohal (1154 m ASL)			Kothi (2474 m ASL)		
Days	PM_{10} ($\mu g/m^3$)	Analyzed samples	Days	PM_{10} ($\mu g/m^3$)	Analyzed samples
24.09.2009	122.9	1,2,3[a]	22.06.2009	83	2,3
13.11.2009	114.2	1,2,3	02.10.2009	69	1,2,3
03.01.2009	112.8	1,2,3	04.07.2009	64.4	1,2,3
22.04.2010	118.9	2,3	06.01.2010	94.7	1,2,3
04.05.2010	99.5	1,2,3	02.01.2010	77.1	1,2,3
01.07.2010	91.5	1,2,3	04.05.2010	69.7	2,3
31.12.2011	92.3	1,2,3	19.05.2011	314.7	1,2
29.12.2011	91.2	1,2,3	05.05.2011	198.1	1,2,3
16.10.2011	80.5	1,2,3	25.11.2011	73.8	1,2,3
14.03.2009	84.1	1,2,3	19.12.2009	29.6	1,2,3
22.06.2009	34.5	1,2,3	20.01.2010	56.2	1,2,3
16.04.2010	90.9	1,2,3	21.06.2010	53.2	1,2,3
22.01.2010	87.9	1,2,3	21.04.2011	69.1	1,2,3
07.01.2011	138.0	1,2,3	30.03.2011	30.3	1,2,3
27.04.2011	80.9	1,2,3	-	-	-
28.09.2009	36.9	1,2,3	-	-	-
19.10.2010	36.3	1,2,3	-	-	-
06.10.2011	43.7	1,2,3	-	-	-

[a] 1,2,3 under columns third and six represent exposed filter paper for 8 hourly duration from 0 h Indian Standard Time (IST) to 0800h IST; 0800h IST to 1600 h IST and from 1600 h IST to 2400 h IST respectively.

Rows from serial number 1 to 9 indicate pollution episode days throughout the year, from 10 to 15 episodes during different seasons and 16 to18 indicate samples during local Kullu Dusshera festival.

- indicates no samples during *Kullu Dusshera* festival at distant location- Kothi.

Table 2. Extracted water soluble ionic components from the exposed PM_{10} ($\mu g/m^3$) filter papers at Mohal and Kothi from 2009 to 2011.

Study site/values	Cations					Anions				Transition metals			
Mohal	Na^+	NH_4^+	Mg^{2+}	Ca^{2+}	K^+	F^-	Cl^-	SO_4^{2-}	NO_3^-	Zn^{2+}	Co^{2+}	Cu^{2+}	Cd^{2+}
Average	1.14	0.84	0.09	1.51	0.50	0.34	3.16	5.56	2.67	0.26	0.01	0.01	0.02
Maximum	2.82	3.04	0.20	3.01	1.35	0.50	6.04	21.53	5.61	0.95	0.01	0.02	0.03
Minimum	0.06	0.12	0.05	0.40	0.20	0.18	1.86	0.73	0.79	0.02	0.01	0.00	0.01
%[a]	7	5	1	9	3	2	20	34	17	2	0	0	0
NSS[b]	-	-	–1366	12	–164	-	58	76	-	-	-	-	-
Kothi													
Average	0.98	0.64	0.06	0.83	0.27	0.25	2.48	2.25	1.28	0.10	0.00	0.00	-
Maximum	1.72	1.09	0.09	0.94	1.08	0.36	3.65	12.44	5.11	0.55	0.00	0.00	-
Minimum	0.04	0.19	0.03	0.72	0.14	0.17	1.71	0.42	0.56	0.02	0.00	0.00	-
%[a]	11	7	0	9	3	3	27	25	14	1	0	0	-
NSS[b]	-	-	–1783	–36	–318	-	54	49	-	-	-	-	-

[a] Percent of the total ionic concentrations.
[b] Non Sea Salt (NSS) fraction.

presence of sulphate and nitrate anions. The acid neutralizing capacity of different cations was estimated by calculating the Neutralization Factor in respect of the particular cations (Fig. 3). These factors were calculated by considering major acidifying anions in the aerosols such as NO_3^- and SO_4^{2-} and major acid neutralizing cations such as Ca^{2+}, NH_4^+, Mg^{2+} and K^+. The role of Cl^- and Na^+ in alkalinity is negligible since their marine origin is basically the sea in the form of sea salt, that is neutral.

The order of neutralizing factors stands to be: $Ca^{2+} > NH_4^+ > K^+ > Mg^{2+}$, assuming their origin from crustal sources (Tiwari *et al.*, 2011). However, it is also found that these have a minor role to play in neutralizing the aerosol acidity. After calculating the neutralization factors for different cations, the ratio NP/AP was calculated to check the overall effect of neutralizing components with respect to the acidic components. The NP/AP ratio calculated for Mohal and Kothi was 0.35 and 0.22, respectively. It indicates that acidic components are dominating over the alkaline components. The acidity generated by sulphate and nitrate is not neutralized by calcium and ammonium so aerosols remain acidic in nature.
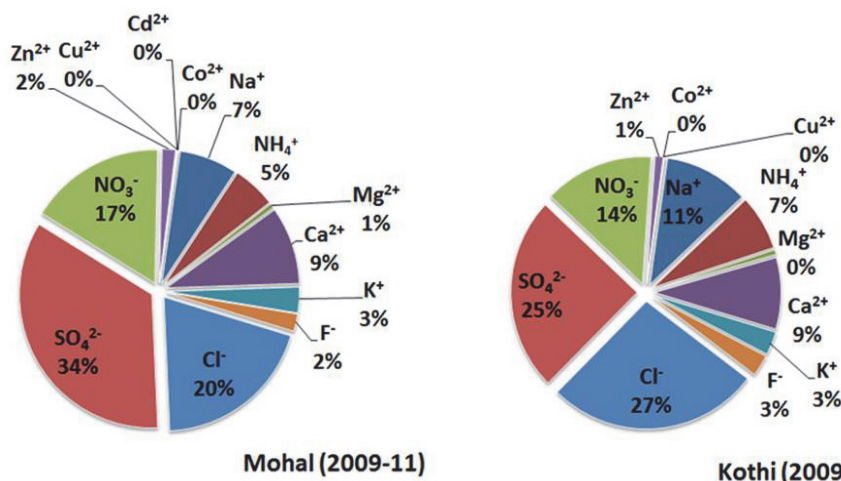
Fig. 2. The concentration of water soluble ions at Mohal and Kothi during 2009–2011.

Table 3. Ratio between different water soluble ionic components.

Ratio between	Mohal	Kothi
NO_3^-/SO_4^{2-}	0.50	0.56
NH_4^+/NO_3^-	0.29	0.50
NH_4^+/SO_4^{2-}	0.15	0.28
$(Ca^{2+} + NH_4^+)/(NO_3^- + SO_4^{2-})$	0.27	0.41
$(NO_3^- + Cl^-)/SO_4^{2-}$	1.08	1.64

Marine Contribution and Non-Sea Salt (NSS) Fraction

Here, Table 4 represents the comparison of equivalent concentration ratios for chloride, potassium, calcium and sulphate at Mohal and Kothi, with respect to sodium in water soluble PM_{10} filter papers and corresponding ratios in sea water. These ratios are the highest at both the sites indicating predominance of non-marine contributions. While for Mg^{2+}/Na^+ the equivalent concentrations ratio at Mohal

and Kothi is 0.07 and 0.06 respectively (see Table 4), and the NSS value calculated for Mg^{2+} is also below 50% indicating their marine source (see Table 2).

After calculating the non-sea salt fraction for Mohal, it was found more than 50% of the total ions for chloride, calcium and sulphate except magnesium and potassium. While for Kothi, it is more than 50% for chloride and sulphate, showing that these were of non-marine origin. This may reflect emissions from burning waste, industrial and other anthropogenic sources.

Factor Analysis and Correlation Matrix

Correlation between elements from the same sources suggests that the samples are related to instability in the same air masses, i.e., inter-airmass instability (Tiwari *et al.*, 2011). While correlation between elements having different sources suggests that samples are related to water soluble ionic components arising out of instability in different
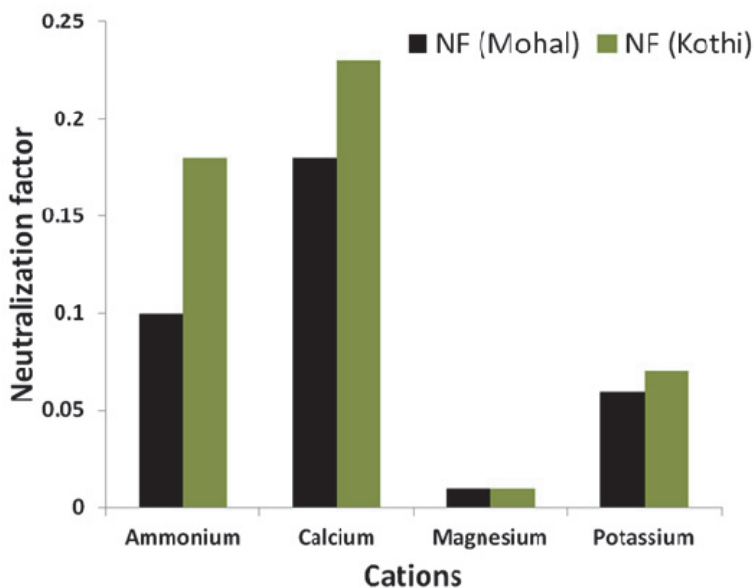

Fig. 3. The neutralization factors for different cations at Mohal and Kothi.

Table 4. Comparison of equivalent concentrations ratios of various ionic species to Na^+.

Study sites	$\left[\dfrac{Cl^-}{Na^+}\right]$	$\left[\dfrac{Mg^{2+}}{Na^+}\right]$	$\left[\dfrac{K^+}{Na^+}\right]$	$\left[\dfrac{Ca^{2+}}{Na^+}\right]$	$\left[\dfrac{SO_4^{2-}}{Na^+}\right]$
Mohal	2.77	0.07	0.43	1.32	4.88
Kothi	2.53	0.06	0.27	0.84	2.29
Amsterdam Island[a]	1.20	0.222	0.0219	0.0464	0.120

[a] after Keene *et al.* (1986).

interacting air masses, i.e., inter-airmass instability. Karl Pearson's correlation coefficient for ionic species is calculated for all the values obtained from the PM_{10} filter papers. All the ionic values of the exposed filter papers were taken into account for that particular day.

Within the principal component analysis, data were subject to a Varimax rotation, which maximizes the variance to obtain a pattern of loading to each factor. Factor loadings are the correlations of each variable with the factor. In this case, the factor analysis is calculated by taking the daily average of ions (drawn from three exposed filters, each sampling for eight hours, during a continuous 24 hour period; Table 5). Two factors have been found in this analysis, giving each variable a loading with each factor. The variable listed within the same factor might have the same origin. Loadings greater than 0.50 mean can be considered to be statistically significant. Loadings with the variance were extracted by the factors (Eigen value > 1) and correlation results are shown in the Tables 6 and 7.

The correlation between ions and the two principal factors at the 95% significance level represents 96% of the total variance in this study. The first factor at Mohal explains 75.59% of the total variance, highly loaded with NH_4^+, K^+, F^-, Cl^- and Zn^{2+}, which indicates availability of anthropogenic species in PM_{10} filters, and for Kothi the first factor explains 45.41% of the total variance, highly loaded with K^+, SO_4^{2-}, NO_3^- and Zn^{2+}, while Mg^{2+} and Ca^{2+} show less of a contribution. The higher loading of these ions in the factor analysis indicates that anthropogenic activities are the probable sources; like fossil fuel burning by industries, exhaust emissions from vehicles, and fires in the forests and open waste burning in the hill towns and spots.

The second factor has high loading for NO_3^-, K^+, Na^+, while Zn^{2+}, Mg^{2+} and F^- show lower values. This factor explains 20.7% of the total variance of the data at Mohal indicating its main origin from crustal sources. Although the zinc and fluoride are significant in both the factors indicating composite sources. The soil is the other major source of nitrate which is available in the atmosphere in the form of $Ca(NO_3)_2$ (Kulshrestha *et al.*, 2005). High loading of NO_3^- in the first factor also suggests that a large proportion of NO_3^- might reflect vehicle exhaust emissions and biomass burning (Budhavant *et al.*, 2009). Soil is also a main contributor of N_2O accounting for some 65% of the total emissions as a result of microbial process, while nitrogenous fertilizers may also contribute directly and indirectly to atmospheric N_2O (Tiwari *et al.*, 2010). At Kothi, the second factor explains 23.48% of the total variance, highly loaded with Cl^-, F^- and NH_4^+ but less with Mg^{2+}.

While the third factor at Kothi is loaded with Ca^{2+} and F^- but less with Na^+ and Cl^-, accounting for 13.77% of the total variance indicating their origin from natural sources such as soil and human and animal excrement.

Extraction Method: Principal Component Analysis

With a purpose to correlate the results with possible sources of different ions, Principal Component Analysis through SPSS software was used under the present study. The ions F^- and K^+ suggest that their sources are from biogenic activities, soils and burning of fossil fuels in a rural environment. The main energy sources for cooking food in the Kullu valley are wood and straw burning, which produce a large amount of potassium. In this Himalayan region, other anthropogenic activities such as biomass burning also produce fluoride and potassium. Whilst mining and incineration are the possible sources of zinc. The uses of fertilizers in the farming, human and animal excreta are the sources of ammonium aerosols. Whereas chloride is sourced from wood burning and tobacco smoking. The ions such as NH_4^+, NO_3^- and SO_4^{2-} in the atmosphere are generally assumed to be the secondary fine particles produced from gas to particle conversion of NH_3, NO_x and SO_x and hence their source can be identified as the secondary pollutants (Shukla and Sharma, 2008).

At Mohal, the first factor in Table 5 explains 75.59% of the total variance, highly loaded with NH_4^+ (0.986), K^+ (0.685), F^- (0.935), Cl^- (0.919) and Zn^{2+} (0.969) indicating the influence of anthropogenic activities on PM_{10} concentration. Probable sources are from vehicle emissions and forest/waste burning. The second factor has high loading for NO_3^- (0.800), K^+ (0.727) and Na^+ (0.499); while Zn^{2+} (0.245), Mg^{2+} (0.213) and F^- (0.174) show low values (see Table 5). This factor explains 20.7% of the total variance of the data indicating crustal sources. The zinc and fluoride show the significant loading in both the factors indicating composite sources.

At Kothi, the first factor explains 45.41% of the total variance, highly loaded with K^+ (0.981), SO_4^{2-} (0.965), NO_3^- (0.953) and Zn^{2+} (0.948), while lower values are found for Mg^{2+} (0.622) and Ca^{2+} (0.621) indicating the influence of anthropogenic activities in the region. The second factor had high loading of Cl^- (0.857), F^- (0.660), NH_4^+ (0.628) but less Mg^{2+} (0.551). On the other hand, the third factor is highly loaded with Ca^{2+} (0.702) and F^- (0.691) but less with Na^+ (0.475) and Cl^- (0.691) showing their origin from natural sources such as soil and excreta from humans and animals.

The meteorological parameters at Mohal show that the maximum prevailing wind directions blow from the north-

Table 5. Factor analysis of ionic components through Principal Component Analysis at Mohal[a] and Kothi[b].

Ions	Component Matrix				
	1[a]	2[a]	1[b]	2[b]	3[b]
Sodium (Na^+)	−0.866	0.499	−0.235	−0.648	0.475
Ammonium (NH_4^+)	0.986	−0.168		0.628	−0.349
Magnesium (Mg^{2+})	−0.976	0.213	0.622	0.551	
Calcium (Ca^{2+})	−0.955	-	0.621		0.702
Potassium (K^+)	0.685	0.727	0.981		−0.135
Fluoride (F^-)	0.935	0.174		0.660	0.691
Chloride (Cl^-)	0.919	−0.227		0.857	0.130
Sulphate (SO_4^{2-})	−0.728	−0.657	0.965	−0.184	
Nitrate (NO_3^-)	−0.561	0.800	0.953	−0.141	−0.103
Zinc (Zn^{2+})	0.969	0.245	0.948		
Eigen Value	7.55	2.07	4.542	2.349	1.377
% Variance	75.59	20.71	45.417	23.488	13.774
Cumulative	75.59	96.31	45.417	68.906	82.680

west or south-east directions, and at Kothi the maximum wind directions blow from a northerly direction. Winds associated with low pressure systems over the Bay of Bengal or the easterly winds near the foothills of the Himalayas could carry pollutants further inland from the industrial belt located in the central part of India. Concentrations of NH_4^+ and SO_4^{2-} were found to be higher when wind blows from the south-east direction (emissions from the power plants located in the states of the Eastern Uttar Pradesh and the northern Madhya Pradesh) compared to the south-west (excreta of humans and animals) (Norman *et al.*, 2001).

Correlation coefficients of chemical species in water soluble PM_{10} filter paper samples at Mohal show significant paired associations, less than 1%, for: Mg^{2+}-NH_4^+, K^--NH_4^+, F^--NH_4^+, Cl^--NH_4^+, SO_4^{2-}-NH_4^+, Ca^{2+}-Mg^{2+}, F^--Mg^{2+}, F^--Ca^{2+}, Cl^--K^+, SO_4^{2-}-K^+, NO_3^--K^+, Zn^{2+}-K^-, Cl^--F^-, NO_3^--F^-, NO_3^--Cl^-, Zn^{2+}-SO_4^{2-} and Zn^{2+}-NO_3^- (see Table 6). While moderate paired associations, with significance levels less than 5% were found for: Ca^{2+}-NH_4^+, SO_4^{2-}-Mg^{2+} and F^--K^-.

At Mohal, the correlation of sulphate and the ammonium ion is strong (r = 0.65), while nitrate with ammonium is weak. So, whilst ammonium sulphate $(NH_4)_2SO_4$ and ammonium nitrate (NH_4NO_3) are both formed, the probability of ammonium sulphate formation is greater than ammonium nitrate. The molar ratio of NH_4/SO_4 is 0.15 and 0.28 at Mohal and Kothi, respectively. A ratio of less than one, meaning a smaller atmospheric presence of the ammonium ion means less neutralization of H_2SO_4, consequently resulting in a greater influence of sulphuric acid (Eq. (7)).

$$NH_3\ (g) + HNO_3\ (g) \rightarrow NH_4NO_3 \qquad (7)$$
$$2NH_3\ (g) + H_2SO_4\ (aq) \rightarrow (NH_4)_2SO_4\ (aq)$$
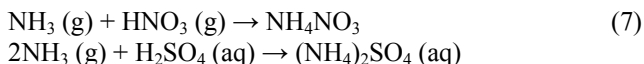
In Table 6, F^- shows a good correlation with Mg^{2+} (r = 0.695) indicating its soil sourcing. Cl^- shows a positive correlation with K^+ (r = 0.403) indicating an anthropogenic origin such as wood burning, while a positive correlation with F^- (r = 0.708) primarily indicates an anthropogenic source such as biomass burning, and a lesser contribution of crustal/ soil sources. SO_4^{2-} showed good correlation with K^+ (r = 0.718), Mg^{2+} (r = 0.592) and NH_4^+ (r = 0.651) indicating coal,

wood and other biomass fuel burning sources. Also, Mg^{2+} shows a good correlation with NH_4^+ (r = 0.826) indicating combined anthropogenic sources.

Correlation coefficients of chemical species obtained in water soluble PM_{10} filter paper samples at Kothi show strong paired associations, at a significance level less than 1%, for: K^--Na^+, SO_4^{2-}-K^+, NO_3^--K^+, NO_3^--SO_4^{2-}. Whilst moderate strength paired associations, with significance levels less than 5%, occur for: SO_4^{2-}-Na^+, K^+-Mg^{2+}, SO_4^{2-}-Mg^{2+}, NO_3^--Mg^{2+} and NO_3^--Ca^{2+} (see Table 7). The remaining species which were not significantly correlated with each other suggest their diverse source regions.

The correlation of calcium with the nitrate ion (r = 0.82) indicates the possible route for the formation of calcium nitrate, $Ca\ (NO_3)_2$ as in Eq. (8):

$$CaCO_3\ (aq) + 2HNO_3\ (g) \rightarrow Ca\ (NO_3)_2(s) + H_2O + CO_2\ (g) \qquad (8)$$
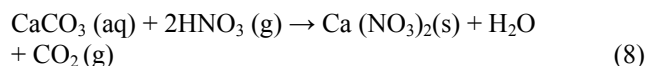
This reaction is the route for forming the coarse fraction of inorganic secondary particles (Sharma *et al.*, 2007). The reaction rate of $CaSO_4$ is less than that of $(NH_4)_2SO_4$ aerosols. As long as a sufficient amount of ammonia is available for neutralization of H_2SO_4 and HNO_3, fine mode $(NH_4)_2SO_4$ and NH_4NO_3 will be formed. It is only when an insufficient amount of NH_3 is present, coarse mode sulphate and nitrate is formed instead.

In Table 7, SO_4^{2-} shows strong correlation with K^+ (r = 0.932) and Mg^{2+} (r = 0.707) indicating their sourcing mainly from the burning of coal, wood and biomass. Cl^- shows good correlation with F^- (r = 0.545) indicating a sourcing from anthropogenic activities. NO_3^- showed strong correlation with Ca^{2+} (r = 0.829) indicating its source from vehicle emissions. NO_3^- also shows good correlation with K^+ (0.900) and SO_4^{2-} (0.922) indicating coal burning in nearby restaurants (*Davas*), and wood burning at Kothi.

AIRMASS BACK TRAJECTORIES

The composition of ambient aerosols and their impacts are influenced by their source and pathway. In order to

Table 6. Karl Pearson's correlation coefficient of water soluble ionic components at Mohal.

	Na^+	NH_4^+	Mg^{2+}	Ca^{2+}	K^+	F^-	Cl^-	SO_4^{2-}	NO_3^-	Zn^{2+}
Na^+	**1**									
NH_4^+	−0.636**	1								
Mg^{2+}	−0.108	**0.826****	1							
Ca^{2+}	−0.067	**0.569***	**0.847****	1						
K^+	−0.014	**0.699****	0.390	0.126	1					
F^-	−0.036	**0.774****	**0.695****	**0.626****	**0.316***	1				
Cl^-	0.246	**0.714****	0.298	0.232	**0.403****	**0.708****	1			
SO_4^{2-}	0.029	**0.651****	**0.592***	0.323	**0.718****	0.025	−0.075	1		
NO_3^-	0.143	0.264	0.222	0.374	**0.594****	**0.480****	**0.566****	0.081	1	
Zn^{2+}	0.082	0.285	−0.100	−0.208	**0.888****	0.105	**0.254**	**0.532****	**0.531****	1

****.** Correlation is significant at the 0.01 level (2-tailed).
***.** Correlation is significant at the 0.05 level (2-tailed).

Table 7. Karl Pearson's correlation coefficient of water soluble ionic components at Kothi.

	Na^+	NH_4^+	Mg^{2+}	Ca^{2+}	K^+	F^-	Cl^-	SO_4^{2-}	NO_3^-	Zn^{2+}
Na^+	**1**									
NH_4^+	.^{a}	1								
Mg^{2+}	0.113	.^{a}	1							
Ca^{2+}	0.508	.^{a}	0.956	1						
K^+	**0.589****	−0.713	**0.752***	0.783	1					
F^-	−0.142	−0.808	0.121	−0.332	−0.066	1				
Cl^-	0.086	0.215	0.196	−0.010	0.149	**0.545****	1			
SO_4^{2-}	**0.499***	−0.852	**0.707***	0.717	**0.932****	−0.251	−0.123	1		
NO_3^-	0.395	−0.892	**0.789***	**0.829***	**0.900****	−0.142	−0.101	**0.922****	1	
Zn^{2+}	.^{a}	.^{a}	.^{a}	.^{a}	.^{a}	.^{a}	.^{a}	.^{a}	.^{a}	1

a. Cannot be computed because at least one of the variables need constant.
**. Correlation is significant at the 0.01 level (2-tailed).

know the possible transport sources of aerosols, the 'HYbrid Single Particle Langrangian Integrated Trajectory' model (HYSPLIT) is used to study the airmass back trajectories (Draxler and Rolph, 2010).

Particulate Pollution during High Pollution Episodes at Mohal

For Mohal, seven-day back trajectories are established at three atmospheric altitudes (1500 m, 2500 m and 4000 m AGL). These trajectories strongly demonstrate that during high pollution episode days, dust is carried from the African and Asian continents. High pollution days during winter months also show wind trajectories coming from the Indo-Gangetic and Punjab Plains of India. In the case of Mohal, trajectories are given for: 13rd November 2009, 31st December 2011, 1st July 2010 and 29th December 2011 (Fig. 4). Calcium ion concentrations were high during these days, for example, it was 1.45 μg/m^3 on 31st December 2013 and 2.11 μg/m^3 on 1st July 2010. The back trajectories show that the dust is transported from the Great Sahara Desert, Middle Eastern Countries and Thar Desert to the Kullu Valley, thereby additionally contributing fine particles to the locally sourced pollutants. Also, the level of gaseous pollutants, like sulphur dioxide and ammonia, seem to be influenced during these days. The major source of pollution during the months of October-November was considered to be biomass burning, coincident with post-harvest crop residue burning.

Particulate Pollution during the Kullu Dusshera Festival at Mohal

During the Kullu Dusshera festival period, the wind trajectories in this area are typically originating from the African desert and the Eastern part of India. The trajectories are again established at three altitudes (1500 m, 2500 m and 4000 m AGL). The high value of sulphate (5.87 μg/m^3) on October 19, 2010 may reflect long range airmass transport from the Eastern part of India, where coal fired power plants operate (Singh *et al.*, 2007). During this day, the concentration of other ions were: NO_3^- (0.92 μg/m^3), K^+ (0.40 μg/m^3) and NH_4^+ (0.28 μg/m^3). Local sources also contribute to particulate and gaseous pollutants during these days due to heavy inflow of vehicles in association with those visiting the festival. The trajectories are drawn for 28th October 2009, and 19th October 2010 (Fig. 5).

Particulate Pollution Episodes and Its Long Range Transport Sources during Different Seasons at Mohal and Kothi

Keeping in mind the altitude of the study region, the back trajectories were established for both sites. These trajectories at Mohal were drawn from AGL for winter and summer seasons at three altitudes: 1500 m, 2500 m and 4000 m AGL. During the summer season, airmass trajectories
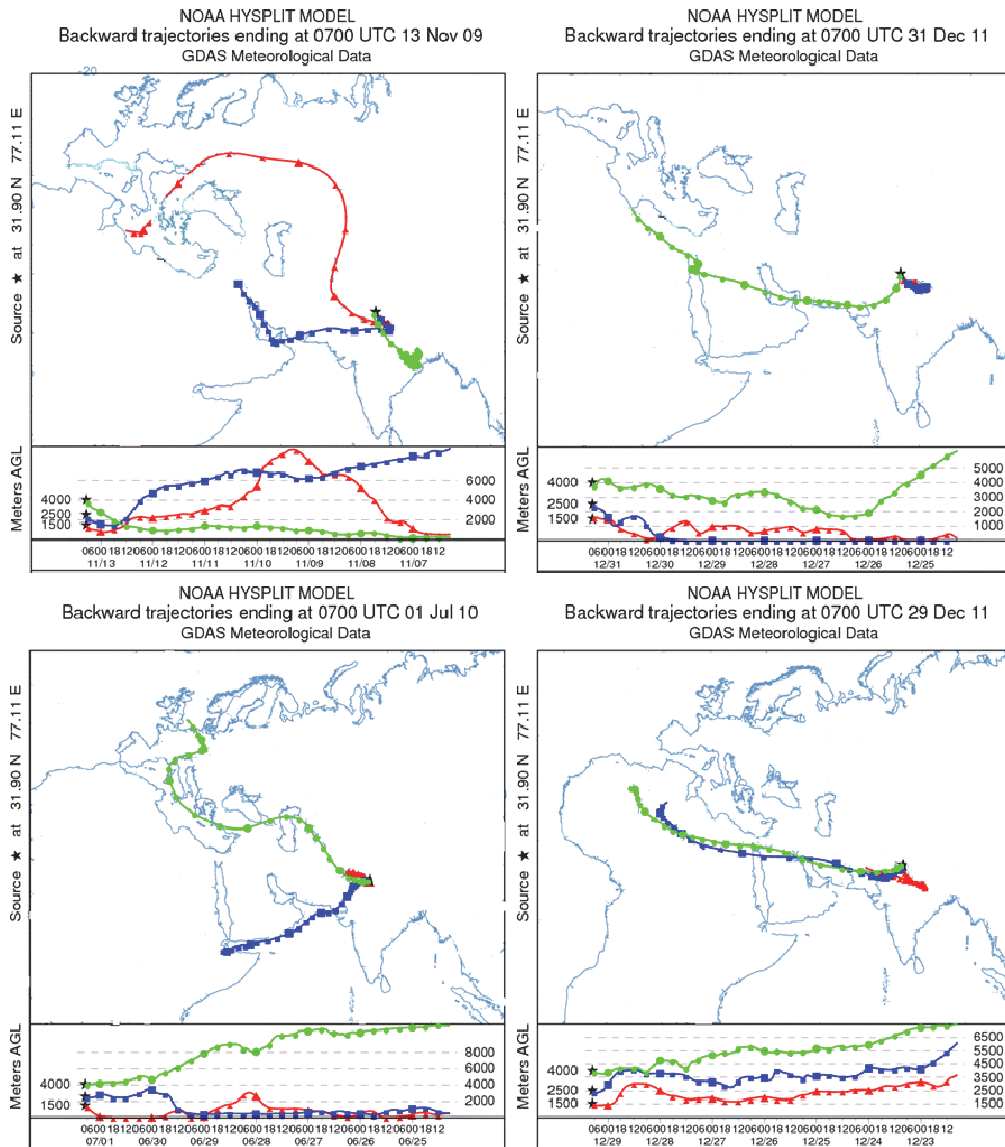
Fig. 4. Back trajectories drawn through HYSPLIT model during high pollution episodes at Mohal.
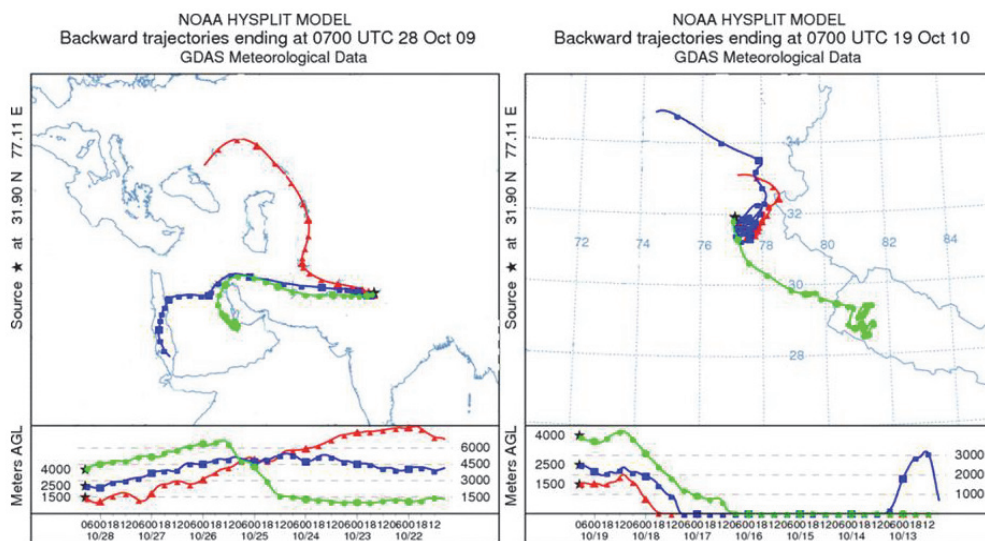

Fig. 5. Back trajectories drawn through HYSPLIT model during Dusshera festival at Mohal.

were coming from the deserts of Africa and Asia. Trajectories corresponding to higher pollution load days were: 14th March 2009, 22nd June 2009, 7th January 2011 and 27th April 2011 (Fig. 6). Calcium ion concentrations were also high during these days, being: 2.38 µg/m^3 on 22nd June 2009 and 3.01 µg/m^3 on 27th April 2011. Seven-day back trajectories for Kothi were established at three alternate altitudes: 2500 m, 3500 m and 5000 m AGL. The trajectories are shown for 2nd January 2010, 4th May 2010, 5th May 2011 and 25th November 2011 (times of elevated pollution load) (Fig. 7). Calcium ion concentrations for Kothi were also high during these days, being: 0.88 µg/m^3 on 2nd January 2010 and 0.94 µg/m^3 on 4th May 2010.

During pollution episodes, it is observed that the wind trajectories were mostly coming from the Sahara, Danakil, Chalbi, Arab and the Asian deserts. The highest concentration of sulphate was found to be on 4th May 2010 when the wind trajectories were coming from the Sahara and Danakil deserts.

On the other hand, the lowest concentration was observed on 2nd January, 2010 when the wind trajectories were coming through airmass from the Mediterranean Sea followed by dry land.

Particulate Pollution Episodes during Different Seasons at Kothi

During summer seasons at Kothi, the airmass back trajectories were coming from the Karakoram desert of the Central Asia, Danakil desert of Africa and western part of the India which generally carry the dust loaded particles. The trajectories drawn at Kothi for 20th January 2010, 21st June 2010, 21st April 2011 and 30th March 2011 have shown high pollution days (Fig. 8).

HYsplit models show a direction of dust plumes spanning long distances, resulting in particulate pollution in the study region. These data act to corroborate the back trajectories, that originate in the desert areas of the African continent.
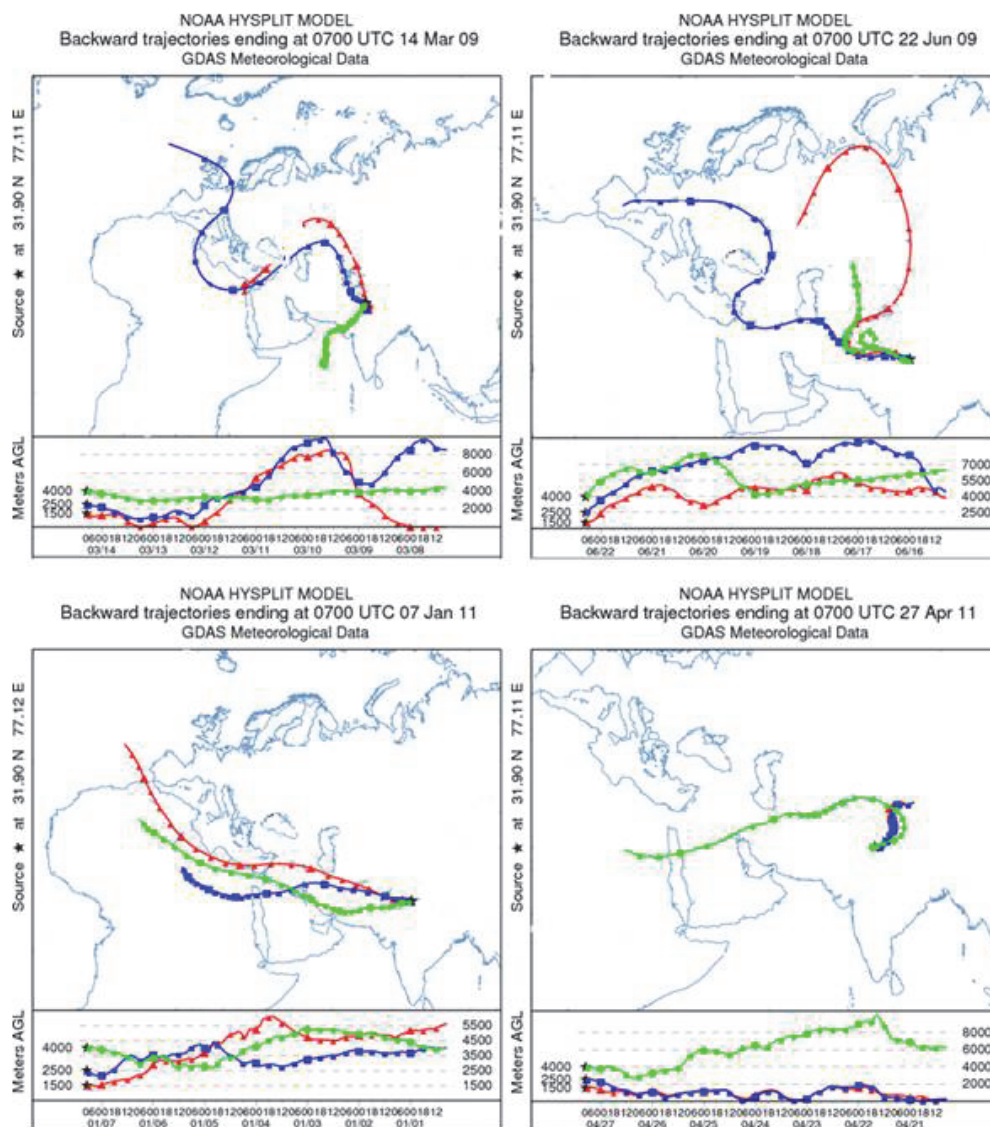
Fig. 6. Back trajectories drawn through HYSPLIT model on the occasion of pollution episodes during different seasons at Mohal.
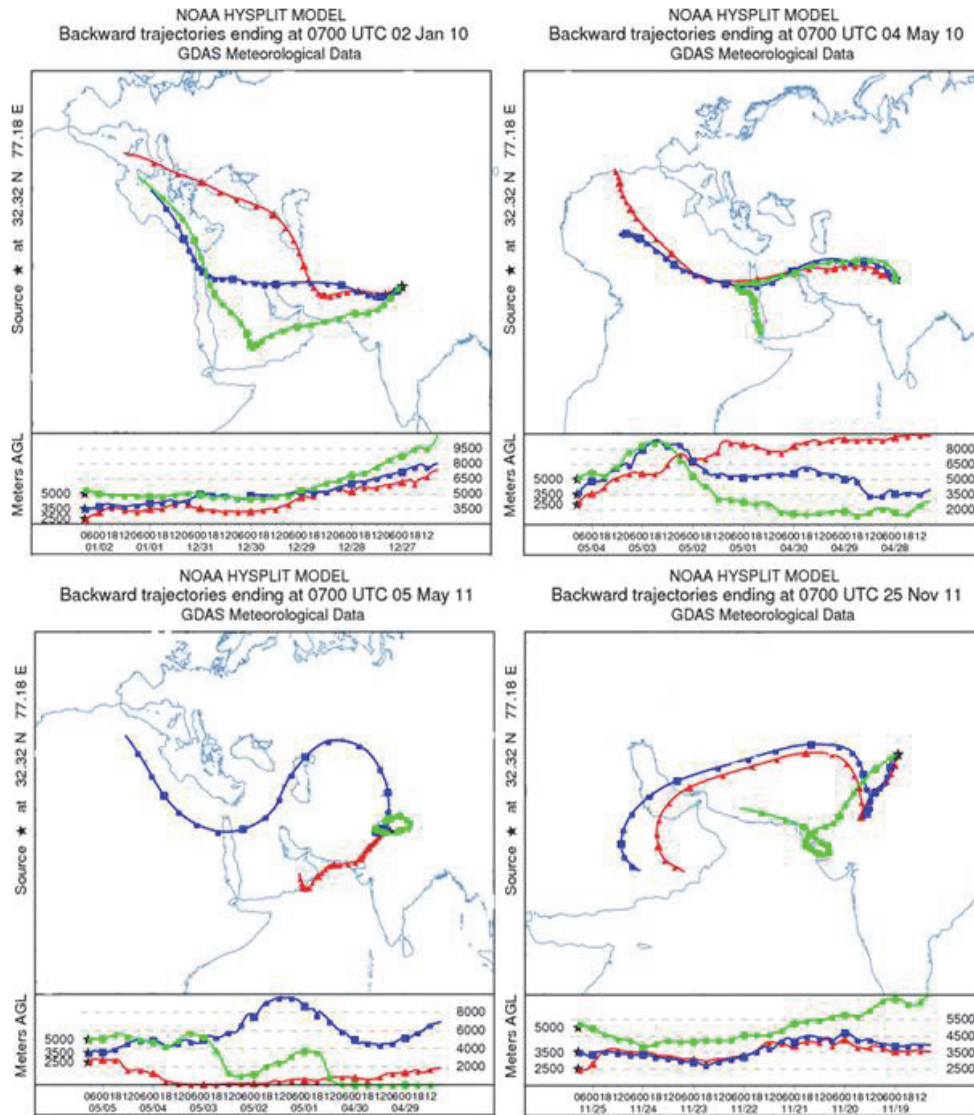
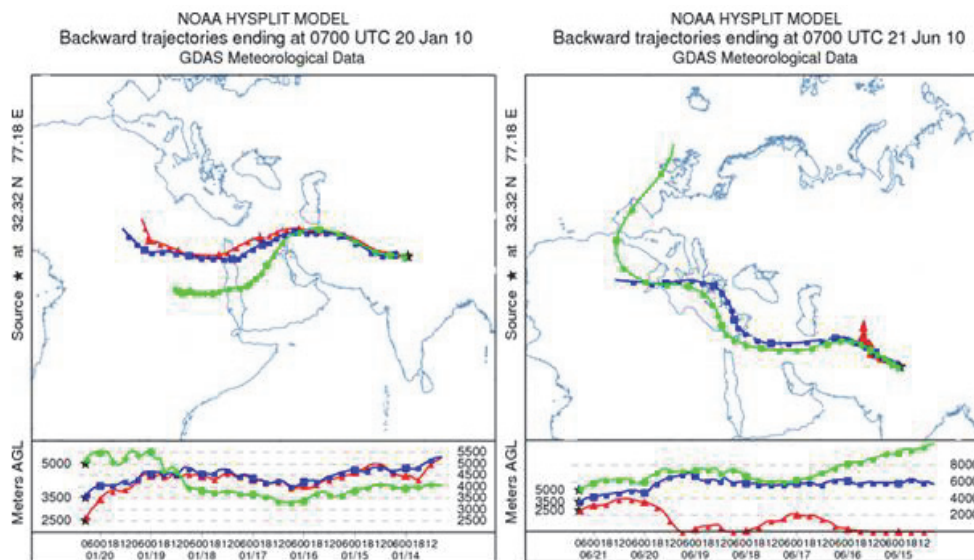**Fig. 7.** Back trajectories drawn during high pollution episodes at Kothi.

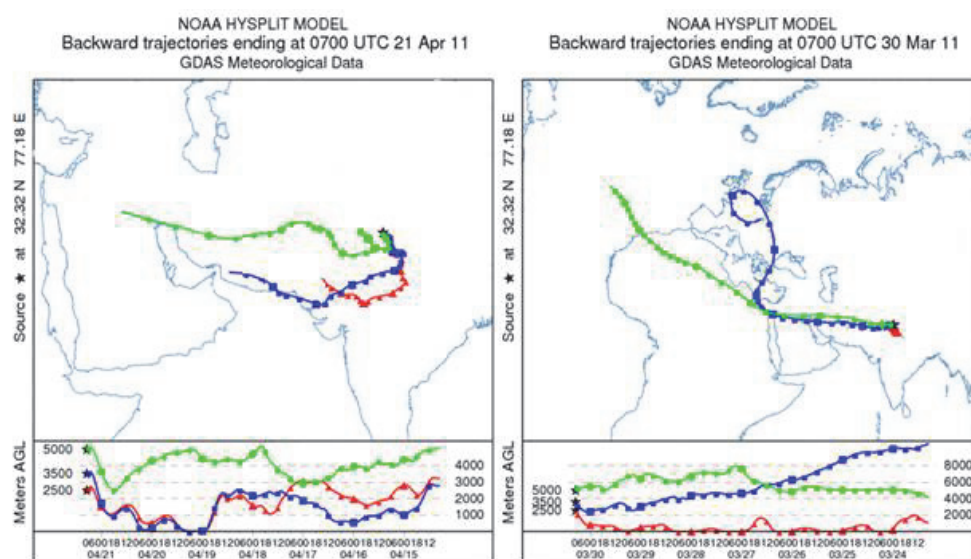**Fig. 8.** Back trajectories drawn during different seasons at Kothi.

Fig. 8. *(continued).*

CONCLUSIONS

The average ratio of $NO_3^- + Cl^-/SO_4^{2-}$ was observed to be 1.08 and 1.64 for Mohal and Kothi, respectively. This indicates that only a small fraction of nitric and hydrochloric acid influence the acidity, given the small margin in excess of unity. The ratios of $Ca^{2+} + NH_4^+/NO_3^- + SO_4^{2-}$ were: 0.27 and 0.41, respectively; indicating a minor role of Ca^{2+} and NH_4^+ ions in the neutralization of acidity in precipitation. The NO_3^-/SO_4^{2-} was observed as 0.5 and 0.56 for Mohal and Kothi, respectively. This indicates contributions of about 66% and 64% of the total sulphuric acid, and 33% and 36% of the total nitric acid to the acidity of aerosols, at Mohal and Kothi respectively. The ratio of NH_4^+/NO_3^- and NH_4^+/SO_4^{2-} was observed as 0.29 and 0.5 and 0.15 and 0.28, for Mohal and Kothi respectively. This indicates less neutralization of sulphuric acid due to predominance of NH_4NO_3 and $(NH_4)_2SO_4$ in the atmosphere. The order of neutralizing factors were observed as $Ca^{2+} > NH_4^+ > K^+ > Mg^{2+}$ assuming that the source of these compounds is of crustal origin. The major source of fluoride and potassium in the Himalayan region is possibly due to biomass burning including that of wood and straw. Anthropogenic activities like mining and incineration of waste are possible sources of zinc. Whilst the presence of chloride might be due to long range transport sources from outside the region (through air masses) as well as from local wood burning and tobacco smoking. Fertilizer use in farming, human and animal excreta are the primary sources of ammonium aerosols. Whereas coal, wood and other biomass burning are the possible sources of magnesium and sulphate aerosols. High pollution episode days, correspond to wind trajectories, blowing from the Eastern India, which have coal-fired power stations emitting sulphate aerosols in the atmosphere. Further, during pollution episodes at Kothi, it is observed that the wind trajectories originating in the Sahara, Danakil and Chalbi deserts of the Africa, Arabia and Asia, increase aerosol concentration.

ACKNOWLEDGEMENTS

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