Measurement of NH$_3$, NO, NO$_2$ and related particulates at urban sites of Indo Gangetic Plain (IGP) of India

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This study presents variability and concentration of ambient NH$_3$, NO and NO$_2$ along with particulate matter (PM$_{10}$) at urban sites of Chandigarh and Delhi of IGP of India (Dec 2010 - Mar 2011). Concentration of NH$_3$ was found as follows: Chandigarh, 0.72 - 22.81 (av 5.17 ± 0.92 µg m$^{-3}$); and Delhi, av 8.54 ± 0.72 µg m$^{-3}$. Concentration of ambient NO (av 13.13 ± 1.50 µg m$^{-3}$) and NO$_2$ (av 5.92 ± 0.38 µg m$^{-3}$) were recorded over Chandigarh. NH$_4^+$ concentration were found as follows: Chandigarh, 2.60 - 4.39 (av 3.41 ± 0.78 µg m$^{-3}$); and Delhi, 6.61 - 14.6 (av 9.91 ± 3.77 µg m$^{-3}$). Concentration of NH$_3$ was significantly correlated with NH$_4^+$ at both of the locations ($r^2$ = 0.87 and $r^2$ = 0.96). NH$_3$/NH$_4^+$ ratios were: Delhi, 0.59 - 1.75 (av 0.86); and Chandigarh, 0.28 - 5.19. A good correlation of SO$_4^{2-}$ and NO$_3^-$ with NH$_4^+$ over Delhi indicates formation of aerosol. Similar correlations were recorded over Chandigarh.

Keywords: Ambient NH$_3$, NO, NO$_2$, PM$_{10}$, Chemiluminescence method, Meteorological parameters

Introduction

Ammonia (NH$_3$) not only plays important role in acidification and eutrophication of aquatic ecosystems$^1$ but also neutralizing atmospheric acids (H$_2$SO$_4$, HNO$_3$ and HCl) and forms inorganic aerosols$^{2-4}$ [(NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and NH$_4$Cl]. Agricultural practices, livestock, transport and industrial activities$^{2,5}$ are different anthropogenic sources of atmospheric NH$_3$, along with natural sources like forest fire and emission from soil. This study estimated concentration of NH$_3$, NO and NO$_2$ and related particulate matter (PM$_{10}$) over Indo Gangetic Plain (IGP) and correlated NH$_3$ concentration with related particulates in the formation of secondary aerosol over IGP.

Experimental Section

Concentrations of ambient NH$_3$, NO, NO$_2$ and PM$_{10}$ (NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$) along with meteorological parameters (temp., RH, wind direction, wind speed etc.) were measured at urban area of Chandigarh and Delhi. NH$_3$ concentration was measured continuously using NH$_3$-analyzer operating based on chemiluminescence method$^3$. PM$_{10}$ samples were collected at IMT, Chandigarh and NPL, New Delhi in weekly intervals (day and night basis) to estimate air mass concentration of particulates and water soluble ionic components (NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$) using Respirable Dust Sampler. Ion concentration of PM$_{10}$ was analyzed by Ion Chromatograph with conductivity detector.

Results and Discussion

Average concentration of ambient NH$_3$, NO and NO$_2$ are summarized (Table 1) along with PM$_{10}$, NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$. Comparisons of average concentration of ambient NH$_3$ over various locations$^{6-11}$ of IGP India are summarized (Table 2) with present study. Average concentration of NO (Table 1) over Delhi was recorded higher than Chandigarh, may be due to influence of heavy traffic, industries, thermal power plants and rapid urban activities in Delhi. Higher NO concentration from NE direction indicates that major source of NO is road traffic, which is 200 m away from observational site$^3$. However, concentration of NO from western direction may be attributed to agricultural field. Average NO$_2$ concentration over Delhi (Table 1) was recorded one order higher than Chandigarh, may be due to heavy traffic, thermal power plants and industries etc. in Delhi.
Ambient NH$_3$ was significantly negatively correlated with ambient temperature ($r^2 = -0.81$) over Delhi during study (Table 3). Similar observations were also reported during winter at Delhi whereas NH$_3$ concentration positively correlated with ambient temperature during summer ($r^2 = 0.79$) and autumn ($r^2 = 0.57$). Day time increase in ambient temperature also attributes to increase in soil temperature which leads to increase soil ammonification and release of NH$_3$ from soil. Concentration of NH$_3$ was significantly positively correlated with NO ($r^2 = 0.96$) and NO$_2$ ($r^2 = 0.92$) over Delhi (Table 3) and similar result was also observed over

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<table>
<thead>
<tr>
<th>Sites</th>
<th>NH$_3$</th>
<th>NO</th>
<th>NO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chandigarh</td>
<td>5.2 ± 0.9</td>
<td>13.1 ± 1.5</td>
<td>5.9 ± 0.4</td>
</tr>
<tr>
<td>Delhi (this study)</td>
<td>8.5 ± 0.7</td>
<td>31.5 ± 4.4</td>
<td>16.6 ± 2.3</td>
</tr>
<tr>
<td>Delhi*</td>
<td>14.4 ± 6.7</td>
<td>15.2 ± 5.8</td>
<td>20.4 ± 6.2</td>
</tr>
<tr>
<td>Delhi*</td>
<td>33.6 ± 9.7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Rampur*</td>
<td>11.6 ± 2.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Agra*</td>
<td>6.6</td>
<td>–</td>
<td>8.6</td>
</tr>
<tr>
<td>Kanpur</td>
<td>16.3 ± 5.0</td>
<td>–</td>
<td>24.1 ± 7.8</td>
</tr>
</tbody>
</table>

*Figures in parenthesis are average values; ± standard deviation
Chandigarh. Sharma et al. have also reported positive correlation of NH$_3$ with NO and NO$_2$ over Delhi.

Positive NO/NH$_3$ ratios over Chandigarh and Delhi indicate influences of NO as one of the source of ambient NH$_3$, which also positively correlated with SO$_4^{2-}$ ($r^2 = 0.90$) and NO$_3^-$ ($r^2 = 0.91$), whereas negatively correlated with ambient temperature ($r^2 = -0.71$) over Delhi (Table 3). Particulate NH$_4^+$ was found positively correlated with SO$_4^{2-}$ ($r^2 = 0.91$) and NO$_3^-$ ($r^2 = 0.96$) over Delhi and similar correlations were observed over Chandigarh (Table 3). Ambient NH$_3$ concentration was significantly correlated with NH$_4^+$ concentration at both the locations ($r^2 = 0.87$ and $r^2 = 0.96$ respectively). Average NH$_4^+/SO_4^{2-}$ and NH$_4^+/NO_3^-$ ratios were computed as 0.40 and 0.38 for Chandigarh respectively, whereas 0.79 and 0.94 for Delhi. A good positive correlation of SO$_4^{2-}$ and NO$_3^-$ with NH$_4^+$ and NH$_3$ over both of observational sites over IGP indicates the formation of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ aerosol$^{3,5}$ during winter. Similarly, NH$_4^+/SO_4^{2-}$ and NH$_4^+/NO_3^-$ ratios also support the formation of inorganic/secondary aerosol over the region.

During day time with increasing UV radiation, NO rapidly converts into NO$_2$ in presence of OD and atmospheric NO$_2$ reacts with hydroxyl radical (OH$^\cdot$) to form nitric acid (HNO$_3$). However, SO$_2$ also reacts with hydroxyl radical (OH$^\cdot$) to form sulphuric acid (H$_2$SO$_4$). During night time, NO$_3^-$ reacts either with NO$_2$ to form N$_2$O$_5$, which reacts, with OH$^\cdot$ to form HNO$_3$ or NO$_3^-$ directly reacts with water vapor to form HNO$_3$. Reaction of HNO$_3$ or H$_2$SO$_4$ with NH$_3$ is reversible and forms NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ respectively. Lower temperature and higher humidity facilitates formation of NH$_4^+$ aerosol$^6$. A significant relationship ($r^2 = 0.92$ at Delhi and $r^2 = 0.90$ at Chandigarh) between NH$_3$ and NO$_2$ indicates (Table 3) formation of HNO$_3$ and simultaneously NH$_4$NO$_3$ in the atmosphere$^6$.

Conclusions

NH$_3$ concentration was measured over Chandigarh [0.72-22.81 (av 5.17 ± 0.92 µg m$^{-3}$)] and Delhi (av 8.54 ± 0.72 µg m$^{-3}$), besides concentrations over Chandigarh of ambient NO (av 13.13 ± 1.50 µg m$^{-3}$) and NO$_2$ (av 5.92 ± 0.38 µg m$^{-3}$). NH$_4^+$ concentration were measured over Chandigarh [2.60-4.39 (av 3.41 ± 0.78 µg m$^{-3}$)] and Delhi [6.61-14.6 (av 9.91 ± 3.77 µg m$^{-3}$)]. Concentration of NH$_3$ was significantly correlated with NH$_4^+$ at both of the locations ($r^2 = 0.87$ and $r^2 = 0.96$). NH$_3$/NH$_4^+$ ratios were calculated over Delhi [0.59-1.75 (av 0.86)] and Chandigarh (0.28-5.19). A good correlation of SO$_4^{2-}$ and NO$_3^-$ with NH$_4^+$ over Delhi and Chandigarh indicates the formation of aerosol.

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References