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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_2SO_4, HNO_3 and HCl) and forms inorganic aerosols[2-4] [$(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl]. 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.

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Results and Discussion

Average concentration of ambient NH_3, NO and NO_2 are summarized (Table 1) alongwith 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.

Table 1—Concentration of NH_3, NO, NO_2, NH_4^+, NO_3^- and SO_4^{2-} (μg m^{-3}) during winter over IGP

Gases and particulates	Delhi	Chandigarh
NH_3	3.69-25.48 (8.54 ± 0.72)*	0.72-22.81 (5.17 ± 0.92)
NO	12.75-69.25 (31.53 ± 4.41)	0.70-28.92 (13.13 ± 1.50)
NO_2	7.26-35.52 (16.62 ± 2.29)	1.55-23.12 (5.92 ± 0.38)
PM_{10}	192.8-288.8 (213.1 ± 15.0)	132.5-186.9 (149.4 ± 25.2)
NH_4^+	6.61-14.60 (9.91 ± 3.77)	2.60-4.39 (3.41 ± 0.78)
NO_3^-	6.84-17.64 (12.51 ± 4.47)	7.10-9.86 (8.47 ± 1.19)
SO_4^{2-}	8.46-11.68 (8.89 ± 1.17)	7.30-10.20 (10.50 ± 1.39)

*Figures in parenthesis are average values; ± standard deviation

Table 2—Comparison of average concentration of ambient NH_3, NO and NO_2 (μg m^{-3}) over IGP

Site	NH_3	NO	NO_2
Chandigarh (this study)	5.2 ± 0.9	13.1 ± 1.5	5.9 ± 0.4
Delhi (this study)	8.5 ± 0.7	31.5 ± 4.4	16.6 ± 2.3
Delhi[7]	14.4 ± 6.7	15.2 ± 5.8	20.4 ± 6.2
Delhi[8]	33.6 ± 9.7	–	–
Rampur[9]	6.7	–	7.3
Agra[9]	6.6	–	8.6
Agra[10]	11.6 ± 2.5	–	–
Kanpur[11]	16.3 ± 5.0	–	24.1 ± 7.8

Table 3—Correlation of NH_3, NO, NO_2 with particulates species along with meteorological parameters

	Locations	PM_{10}	NH_3	NO	NO_2	NH_4^+	SO_4^{2-}	NO_3^-	Temp	RH
PM_{10}	Delhi	1.00								
	Chandigarh	1.00								
NH_3	Delhi	0.56[a]	1.00							
	Chandigarh	0.51	1.00							
NO	Delhi	0.53	0.96[a]	1.00						
	Chandigarh	0.49	0.89[a]	1.00						
NO_2	Delhi	0.43	0.92[a]	0.95[a]	1.00					
	Chandigarh	0.48	0.90[a]	0.78[a]	1.00					
NH_4^+	Delhi	0.76[a]	0.96[a]	0.95[a]	0.87[a]	1.00				
	Chandigarh	0.79[a]	0.87[a]	0.83[a]	0.77[a]	1.00				
SO_4^{2-}	Delhi	0.67[a]	0.90[a]	0.86[a]	0.65[a]	0.91[a]	1.00			
	Chandigarh	0.57[a]	0.83[a]	0.82[a]	0.53[a]	0.87[a]	1.00			
NO_3^-	Delhi	0.79[a]	0.91[a]	0.88[a]	0.71[a]	0.96[a]	0.93[a]	1.00		
	Chandigarh	0.80[a]	0.93[a]	0.91[a]	0.63[a]	0.93[a]	0.92[a]	1.00		
Temp	Delhi	-0.81[a]	-0.71[a]	-0.65[a]	-0.41	-0.80[a]	-0.93[a]	-0.93[a]	1.00	
	Chandigarh	–	–	–	–	–	–	–	–	
RH	Delhi	0.88[a]	0.51	0.45	0.21	0.67[a]	0.79[a]	0.82[a]	-0.95[a]	1.00
	Chandigarh	–	–	–	–	–	–	–	–	–

[a]Significant at $P < 0.05$

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[3] 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[3]. 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

Chandigarh. Sharma *et al*[3] have also reported positive correlation of NH_3 with NO and NO_2 over Delhi.

Positive NO/NH_3 ratios over Chandiagrh 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 $(NH_4)_2SO_4$ and NH_4NO_3 aerosol[4,5] 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 O^1D and atmospheric NO_2 reacts with hydroxyl radical ($OH^•$) to form nitric acid (HNO_3). However, SO_2 also reacts with hydroxyl radical ($OH^•$) to form sulphuric acid (H_2SO_4). During night time, NO_3^- reacts either with NO_2 to form N_2O_5, which reacts, with $OH^•$ to form HNO_3 or NO_3^- directly reacts with water vapor to form HNO_3. Reaction of HNO_3 or H_2SO_4 with NH_3 is reversible and forms NH_4NO_3 and $(NH_4)_2SO_4$ 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_4NO_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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