



## AMBIENT AIR INTERACTIONS BETWEEN PARTICULATE MATTER AND GASES OF COMBUSTION

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### ABSTRACT

The study was primarily initiated to explore possibility of chemical transformation of NO<sub>x</sub> to nitrates and get adsorbed onto the fine particle surfaces based on secondary data from various sources. This required manipulations of secondary data to find correlations between PM, PM-nitrates and NO<sub>x</sub>. Data were downloaded from EPA's website (Environmental Protection Agency, USA; www.epa.gov), which include 24 hours PM<sub>10</sub>, PM<sub>2.5</sub>, PM<sub>1</sub> and NO<sub>x</sub> concentrations. The corresponding PM-nitrate concentrations were obtained by manipulations made on various graphs of ambient particulate composition. Subsequently, coefficients of correlation among various parameters were calculated. It was observed that stronger correlations are obtained between PM-nitrates and NO<sub>x</sub> as size of particle is decreased. A similar trend was observed during an air quality monitoring exercise in Delhi. The ambient interactions between PM and NO<sub>x</sub> further imply that ambient NO<sub>x</sub> values obtained during air pollution monitoring are superficial and, thus, there is a need to revise the existing PM-NO<sub>x</sub> standards. From the health point of view, the synergistic interactions between PM and NO<sub>x</sub> have more deleterious effect on human health than NO<sub>x</sub> alone.

### INTRODUCTION

The review of literature suggests possibility of chemical transformation of NO<sub>x</sub> to nitrate (NO<sub>3</sub><sup>-</sup>), which gets adsorbed onto the fine particle surfaces (Schauer et al. 1996). This could be construed by the fact that over the years, in spite of increased level of NO<sub>x</sub> emissions in the major cities of the world, the ambient NO<sub>x</sub> levels have remained more or less unchanged. This is evident from various studies carried out in the cities of the US (Magliano et al. 1998), UK (Harrison & Msibi 1994), Australia (Chan et al. 1997), Japan (Kaneyasu et al. 1995) and Europe (Schaap et al. 2004).

The objective of the present paper was to understand the formation of NO<sub>3</sub><sup>-</sup> as a function of NO<sub>x</sub> and discover the correlation trends between particle size and NO<sub>x</sub> based on secondary data, to understand the same. It was hypothesized that the mechanism of formation of NO<sub>3</sub><sup>-</sup> takes place through adsorption onto the surface of fine particles emitted during combustion resulting in these particles acting as sinks for NO<sub>x</sub>. If NO<sub>x</sub> does transform to NO<sub>3</sub><sup>-</sup>, the resultant NO<sub>3</sub><sup>-</sup> levels pose additional health implications (Dockery et al. 1993). Therefore, there is a need to understand NO<sub>3</sub><sup>-</sup> formation in the atmosphere and examine the NO<sub>3</sub><sup>-</sup> levels.

### MATERIALS AND METHODS

The study required compilation of data related to particulate matter and gases concentrations. This entailed reviewing of various air quality journals and websites of EPA and NEERI (National Environmental Engineering Research Institute) for finding pertinent data. Most of the useful data were in graphical and tabular forms. Some data were directly taken whereas some were obtained through mathematical manipulations on graphs wherever viable. From these, coefficients of correlation were

obtained among  $PM_{10}$ ,  $PM_{2.5}$ ,  $PM_1$ ,  $NO_x$ ,  $PM_{10}$  (nitrates),  $PM_{2.5}$  (nitrates) and  $PM_1$  (nitrates). Microsoft Excel was used for finding coefficients of correlation.

## RESULTS AND DISCUSSION

Data for 24 hours  $PM_{10}$ ,  $PM_{2.5}$ ,  $PM_1$  and  $NO_x$  were obtained. From the corresponding particulate matter composition graphs, the PM-nitrate concentrations were found. Subsequently, correlations among various parameters were calculated. Fig. 1 shows the  $PM_1$  concentration and composition at 9 locations in USA. The secondary data and data obtained from various graphs and tables are presented in Table 1 for  $PM_{10}$ ,  $PM_{2.5}$ ,  $PM_1$ ,  $NO_x$ ,  $PM_{10}$  nitrates,  $PM_{2.5}$  nitrates and  $PM_1$  nitrates. Table 2 presents the coefficients of correlation calculated. The arithmetic mean and standard deviation of various air quality parameters for Delhi have been given in Table 3. Table 4 gives the subsequent coefficients of correlation calculated.

The coefficients of correlation between PM nitrates and  $NO_x$  are increasing as the particle size is decreased as is evident from Table 2 and Table 4. This could be attributed to the fact that finer particles have larger surface area and, thus, adsorb more gases. This further implies that the decreased  $NO_x$  concentrations, observed in various cities of the world, is not due to lesser emissions but because of ambient  $NO_x$  interactions with particulate matter. Thus, combustion generated particulate matter act as sink for the liberated gases of combustion. From the health point of view ambient  $NO_x$  interactions with fine particulate matter have more deleterious effect on human respiratory system than  $NO_x$  alone. Thus, there is a need to revise the existing PM- $NO_x$  standards. However, strong correlation between  $NO_3$ -FSP and  $SO_4$ -FSP for Delhi (Shandilya 2002) could be expounded by the fact that both are combustion generated and have same source.

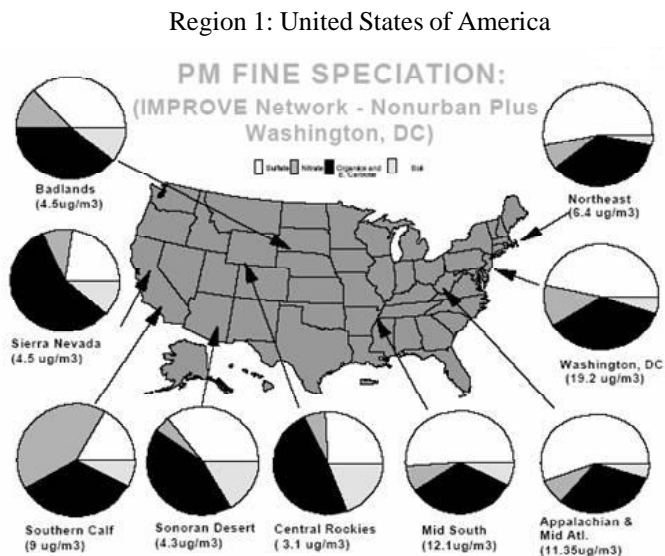


Fig. 1: PM fine speculation (USA).

Source:  $PM_1$  Composition and Sources (Prepared by: Emissions, Monitoring and Analysis Division, Office of Air Quality Planning and Standard, USA; June 16, 1997)

Table 1: Secondary data and corresponding manipulations of various sites in USA (All values are in  $\mu\text{g}/\text{m}^3$ ).

	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>1</sub>	NOx	PM <sub>10</sub> nitrates	PM <sub>2.5</sub> nitrates	PM <sub>1</sub> nitrates
Badlands	48	26	4.5	43.13	3.2	2.86	0.59
Sierra Nevada	142	29	4.5	37.5	7.5	3.82	0.36
Southern California	79	53	9	327	22	18.02	4.05
Sonoran Desert	200	41	4.3	23	12	5.33	0.17
Central Rookies	123	44	3.1	27	7	2.4	0.186
Mid. South	47	43	12.1	104	4.2	3.4	1.1
Appalachian and Mid. Atlantic	48	33	11.35	100	3.8	2.64	0.91
Washington DC	72	38	19.2	145	6.48	3.54	2.4
Northeast	58	37	6.4	43.13	3.48	1.32	0.512

Table 2: Table of coefficients of correlation among various parameters for sites in USA.

	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>1</sub>	NOx	PM <sub>10</sub> nitrates	PM <sub>2.5</sub> nitrates	PM <sub>1</sub> nitrates
PM <sub>10</sub>	1						
PM <sub>2.5</sub>	0.12	1					
PM <sub>1</sub>	-0.486	0.153	1				
NOx	-0.323	0.636	0.472	1			
PM <sub>10</sub> Nitrates	0.367	0.716	-0.06	0.73	1		
PM <sub>2.5</sub> Nitrates	0.069	0.67	0.055	0.87	0.9	1	
PM <sub>1</sub> Nitrates	-0.341	0.6	0.571	0.981	0.68	0.8	1

Region 2: Delhi

Table 3: Air quality monitoring results for sites in Delhi (source: Shandilya 2002).

$\mu\text{g}/\text{m}^3$	NO <sub>3</sub> <sup>-</sup> RSP	NO <sub>3</sub> <sup>-</sup> FSP	NOx	PM <sub>10</sub> RSP	PM <sub>2.5</sub> FSP	SO <sub>4</sub> <sup>=</sup> FSP	SO <sub>4</sub> <sup>=</sup> RSP
AM ± SD	16 ± 2	12 ± 2	72 ± 12	271 ± 39	130 ± 29	24 ± 5	44 ± 11
AM ± SD	10 ± 2	6 ± 1	41 ± 6	204 ± 35	144 ± 39	13 ± 4	24 ± 5
AM ± SD	15 ± 2	11 ± 1	69 ± 11	261 ± 50	160 ± 45	22 ± 5	38 ± 13
AM ± SD	20 ± 2	12 ± 2	135 ± 19	233 ± 65	175 ± 21	28 ± 2	57 ± 3

Table 4: Table of coefficients of correlation among various parameters for sites in Delhi.

CORR	RSP	NOx	FSP	NO <sub>3</sub> <sup>-</sup> -RSP	NO <sub>3</sub> <sup>-</sup> -FSP	SO <sub>4</sub> <sup>-</sup> -RSP	SO <sub>4</sub> <sup>-</sup> -FSP
RSP	1.00						
NOx	0.22	1.00					
FSP	-0.2	0.53	1.00				
NO <sub>3</sub> <sup>-</sup> -RSP	0.67	0.73	0.04	1.00			
NO <sub>3</sub> <sup>-</sup> -FSP	0.15	0.83	0.50	0.69	1.00		
SO <sub>4</sub> <sup>-</sup> -RSP	0.26	0.72	0.39	0.71	0.81	1.00	
SO <sub>4</sub> <sup>-</sup> -FSP	0.10	0.79	0.64	0.58	0.92	0.79	1.00

## CONCLUSION

Increasingly higher correlations between NO<sub>x</sub> and PM-nitrates with decreasing particle size (PM<sub>10</sub> nitrates and NO<sub>x</sub> (0.73), PM<sub>2.5</sub> nitrates and NO<sub>x</sub> (0.87), PM<sub>1</sub> nitrates and NO<sub>x</sub> (0.981)) reinforce our contention that combustion generated particulate matter acts as a sink for ambient NO<sub>x</sub>. Thus, understanding particulate matter and NO<sub>x</sub> interactions is essential in bringing meaningful standards for fine particles and NO<sub>x</sub>, especially in view of their synergistic impact on human respiratory system.

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