VARITION IN SPATIAL PATTERN OF CRITERIA AIR POLLUTANTS BEFORE AND DURING INITIAL RAIN OF MONSOON

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ABSTRACT

Spatial patterns of various criteria air pollutants, like SO_2, NO_2, O_3, and TSP, were study at Shahdara National Ambient Air Quality Monitoring station in Delhi (India) in July 1999. The minimum pollutant concentrations were observed during early morning hours, whereas the highest concentrations were found during the late night hours, which seem to be related with the vehicular emission. Pre-monsoon daily ambient air quality spatial pattern was compared with the spatial pattern during initial and subsequent rain shower of monsoon. These spatial patterns were found to be essentially the same before and during rain, however decrease in SO_2, NO_2 and TSP concentration significantly by 40-45% after initial and subsequent rains of the monsoon was observed,

demonstrating the importance of rainfall in the scavenging of these criteria air pollutants.

Key words: *spatial pattern, air pollutants, SO_2, NO_2, TSP, rain, monsoon, air quality.*

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INTRODUCTION

Most of the cities in developing countries suffer from serious outdoor air pollution due to poor control of industrial emission and due to improper maintenance of vehicles. Pollutants emitted by industries and vehicles adversely affect the health and property of the inhabitants. The air pollutants transported by prevailing winds and dispersed by diffusion become a part of the atmosphere (Lyons et al., 1990; Glen et al., 1996). These pollutants both wet and dry finally, deposited from the atmosphere, and are absorbed on other environmental compartments, such as water, soil or the biosphere. Air pollutants are, thus a part of the atmosphere only for a limited period. Large aerosols and particles fall down due to gravity, while smaller particles coagulate to form larger particle, which also fall down, or precipitated out. Precipitative deposition is generally considered to be the primary mechanism via which airborne compounds

are removed from the atmosphere (Cawse, 1974). Ho et al. (1997) have shown a significant and systematic enhancement between air-water gas exchanges during rainfall. Gases and solid particles absorbed by clouds and /or by raindrops get washed down during rainfall (rain-out and wash-out), which contributes to the cleaning of the atmosphere.

In the present study, various criteria air pollutants were studied at Shahdara National Ambient Air Quality Monitoring (NAAQM) Station in Delhi, India. This station is located at an area, which represents mixed characteristics of industrial, vehicular, and residential sites. The objective of this study includes the assessment of the daily pattern of sulfur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3) and total suspended particulate (TSP) matter, (4 hourly variation for gaseous pollutants and 8 hourly variation in TSP) and the evaluation of the variations in the air quality and **its** spatial pattern, just after the subsequent rain of Monsoon. . The observations were carried out in July 1999. The first showers of monsoon were experienced after mid-July during study period. The pollutant concentrations after first and subsequent rains were also compared with those of just before the rain, to study the washout (precipitation) phenomenon expected to clean the atmosphere.

MATERIALS AND METHODS

Monitoring of criteria pollutants were undertaken at a site adjacent to Jhilmill industrial area and near to heavily travelled road and highway No. 58 in Delhi, situated at $28^0$35' N latitude, $77^0$17'E longitude and 216 m above the mean sea-level. Sampling was performed with the help of a high volume sampler (Envirotech model APM 415), equipped with a gaseous sampling attachment. The sampling inlet was located 25 feet above the ground level, to collect the samples for TSP, SO_2, NO_2, and ozone (O_3). TSP was collected on a 20 cm x 25 cm glass fiber filter (GFF). The sampling schedule for TSP was divided into three shifts of eight hours per day. The flow rate varied from 0.8 to 1.2 m^3/min and finally average flow rate was calculated. For gaseous (SO_2 and NO_2) sampling the impingers were exposed for 4-hour at an impingement rate of one dm^3/min to get six samples in a day. Sampling of ozone was performed during daytime at each interval of one hour, preferably from 9 a.m. to 5 p.m. only, as the ozone formation is sunlight dependent. Sulfur dioxide was analysed by West-Gaeke method on Spectronic-21 spectrophotometer at wavelength of 560 nm . Nitrogen dioxide was analysed by employing the Jacob- Hochheiser (1958) modified method on the same spectrophotometer at wavelength of 540 nm (Harrison et al., 1986; Lodge, 1989; Kartz, 1997). For TSP determination, the weight difference of the GFFs were measured before and after the sampling using a Mettler AT2001 analytical balance. Ozone was indirectly

analysed by measuring the absorbance of tri-iodide ion by the same spectrophotometer at wavelength of 352 nm (Lodge, 1989).

RESULTS AND DISCUSSION

Sulfur dioxide

Sulfur dioxide concentrations in the ambient air in cities of developed countries have mostly decreased in the last two, or three decades, due to the strict emission control, increased use of low sulfur content fuel and industrial restructuring. Consequently, the high SO_2 concentrations in earlier decades have been replaced by annual mean concentration of about 20-40 $\mu g/m^3$ in most cities of the developing countries, and the daily average values rarely exceed 125 $\mu g/m^3$. In developing countries, the annual mean concentration of SO_2 may range from very low levels up to 300 $\mu g/m^3$ in the ambient air (WHO, 1998).

According to the present study, SO_2 concentrations at the monitoring station (Table 1) were below the maximum allowed limit of National Ambient Air Quality Standards (120 $\mu g/m^3$) for industrial areas. During the study period , the four hourly average SO_2 concentrations varied from 1.17 to 30.21 $\mu g/m^3$. The daily average value varied from 4.09±1.3 to 16.1±12 $\mu g/m^3$ (Table 2). The spatial pattern showed the maximum values of SO_2 concentration during the late evening periods,

whereas the minimum value was observed from 12.00 to 4.00 p.m., and in the early morning hours. After 8.00 a.m. the SO_2 concentration increased, however, it showed a slight fall between 12.00 and 4.00p.m. After this period, SO_2 concentration showed an increasing trend and reached its maximum value during the late night monitoring period (Figure 1).

Although the spatial pattern of SO_2 followed the same trend before and during the rain, a sharp decrease was found for the SO_2 concentration during rainfall (Table 3). The results show**s** that there is approximately 38% decrease in the SO_2 concentration during rain (6.48 ± 2.9 $\mu g/m^3$) than before rain ($10.51 \pm 5.2 \mu g/m^3$) in the air.

It has been shown that when SO_2 is present in the air, the dissolved SO_2 can comprise a significant portion of the total sulfur in rainwater (Hales and Dana, 1979; Davis, 1979). The sulfur in the precipitation comes from the sulfate particles scavenged by clouds and raindrops and by the oxidation of SO_2 dissolved in the drops (Freiberg, 1975; Penkett et al., 1979; Barrie and Georgii, 1976). Pena et al., in 1981 reported S(IV) content in the rain samples close to the equilibrium values corresponding with increased drop size and /or reduced SO_2 level in the air.

Applying equilibrium scavenging theory, it is possible to express the rainwater SO_2 content, as a function of the SO_2 concentration of air, the temperature and the free acidity of the rainwater. Many studies (e.g.

Barrie, 1978; Pena et al, 1981) showed that small raindrops in high SO_2 concentration virtually reached equilibrium, and increased considerably with increased drop size and /or reduced SO_2 level in the air. On the base of the above experiments, and the former work cited, a high decrease of **SO_2** concentration can be deduced during rainfall.

Nitrogen dioxide

The concentration of NO_2 can vary to a large extent in the ambient air. Natural background concentration of NO_2 in the ambient air can be <1 $\mu g/m^3$ to >9 $\mu g/m^3$. In several cities, the annual mean concentration ranged from 20-90 $\mu g/m^3$ with hourly maximum concentrations from 75 to 1000 $\mu g/m^3$ (WHO, 1994).

In the present study Nitrogen dioxide concentrations during four hourly monitoring periods varied between 14.27 $\mu g/m^3$ **to** 221 $\mu g/m^3$. The daily average value varied from 23.73±4.3 to 113±50 $\mu g/m^3$ (Table 2). On an average, NO_2 concentration was minimum during early morning monitoring period from 4.00 a.m. to 8.00 a.m. It was also observed that NO_2 concentration increases with the increase in vehicular density, and declines as the vehicle traffic decreases on the roads. Maximum NO_2 concentration were observed during late night monitoring period from 8.00 p.m. to 12.00 p.m. Spatial pattern of NO_2 concentration showed its

second highest value between 8.00 a.m. to 12.00 p.m. during the monitoring period (Figure 2).

The daily average nitrogen dioxide concentration decreased from 68.45± 29.3 μg/m^3 (before rain) to 38.34±7.3 μg/m^3 during rainfall, which means a nearly 44 % washout of the ambient NO_2 concentration (Table 3). Before the rainfall, NO_2 concentration seems to approach the maximum prescribed value for industrial areas, i.e. 120 μg/m^3. Daily spatial pattern followed the same trend before and during rain, although it showed less variation in daily average concentration during rainy periods.

Hubert et al. (1983) calculated the scavenging coefficient (Λ), and washout ratio for nitrogen and sulfur species. The scavenging coefficient is the rate constant for the first order removal of a species, i.e. $(HNO_3)_t = (HNO_3)_0 \exp(-\Lambda t)$, where t denotes the time that increases with the precipitation rate. The washout ratio is defined as the concentration of the precipitated substance to its concentration in air, [i.e. $R = (HNO_3)_p d / (HNO_3)_a$], where the concentration in air is in μg/m^3, and d is the density of air in g/m^3. R decreases when the precipitated amount of the particulates substance increases. Chang (1984) indicates that for a precipitation rate around 1 mm/h, the scavenging of below-cloud HNO_3 vapours by rain of about 40% per hrs. Topol (1986) has also shown that

scavenging of nitrogen species by rain and snow is more important than that of sulfur species.

Ozone

Ozone is formed in the troposphere by photochemical reaction of hydrocarbons and nitrogen oxides, emitted from fuel combustion, and by refuse burning and evaporation from petroleum products and organic solvents. Sunlight (UV radiation) and hot weather conditions promote ground-level O_3 formation. in harmful concentrations. Background concentrations of O_3 in remote and relatively unpolluted parts of the earth are often in the range of 40-70 $\mu g/m^3$, as a one-hour average. In cities and areas downwind of the cities, the O_3 concentration can persist for 8 to 12 hours per day for several days, when atmospheric conditions favours O_3 formation, and /or poor dispersion conditions exist (WHO, 1999).

According to the present study the daily O_3 concentration were below the detection limit of the applied analytical method (20 $\mu g/m^3$). This was due to the cloudy weather with the weak sunlight in the monsoon season. The observed O_3 concentration was, therefore, very low as compared to the hourly standard limit (i.e. 235 $\mu g/m^3$) of United States Environmental Protection Agency.

Total suspended particles

The concentration of particulate matter in the air is highly variable. In most of the cities of world**,** the TSP annual mean concentration were reported to be >100 $\mu g/m^3$, with the level exceeding 300 $\mu g/m^3$ in several cities of China and India. There is no evidence of any overall systematic and significant change in the TSP level. The data from the 1990**'**s shows the increasing as well as decreasing trend in a similar number of cities (WHO, 1999)

During eight hourly monitoring periods, the TSP concentration varied between 85.44 $\mu g/m^3$ to 832 $\mu g/m^3$. The spatial pattern showed an increasing trend for TSP concentration from early morning to late night. The highest daily average concentration of SPM was observed between 4.00 p.m. to 12.00 p.m. monitoring period (Figure 3).

Before rain, the daily average TSP concentration was 350±121 $\mu g/m^3$, which reduced to approximately 40-48 % during the initial rain of monsoon, and reached the daily average concentration of 196±44 $\mu g/m^3$ (Table 3). Before rain, TSP concentration was near the maximum value prescribed by National Ambient Air Quality Standards, but during monsoon period, the washout phenomenon played an important role to keep TSP concentration below 500 $\mu g/m^3$ for industrial sites, which is the maximum permissible level.

CONCLUSION

The spatial patterns of SO_2 and NO_2 showed approximately the same trend as regards the various monitoring periods of the day. Their concentration was found to be minimum during morning hours, which started raising with the increase in number of vehicles on the roads. They showed a slight fall during afternoon period and reached to maximum concentration during late evening hours. The increased values of these pollutants in the late evening period seems to be related with the increased number of heavy traffic (trucks, vans, etc.) at late night. This type of traffic increases in the late evening hours (after 10.00 p.m.) due to restricted entry of heavy vehicles in the metropolitan city of Delhi during daytime. The TSP concentration was found to be maximum during daytime period and starts decreasing in the early morning sampling period. Ozone concentration was found to be below the standard value and the detection limit. Daily ambient air quality spatial pattern showed the almost same behaviour before and during rain, but it had less variation in daily average concentration during rainy periods. Concentration of criteria air pollutants (SO_2, NO_2 and TSP) decreased by 40 to 45% after initial and subsequent rain of the monsoon, which shows that rain plays an important role in the washout of air pollutants.

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Table 1 Average spatial patterns of SO_2, NO_2 and TSP concentrations before and during the starting rain of monsoon with standard deviations.

Day Times / Parameters*		00-04	04-08	08-12	12-16	16-20	20-24	Daily Average
SO_2	**BR**	16.76 ± 12.9	6.06 ± 1.7	10.30 ± 5.3	4.48 ± 2.5	7.80 ± 7.8	17.56 ± 9.9	10.51 ± 5.5
	DR	7.56 ± 5.4	6.79 ± 7.4	9.94 ± 8.5	2.94 ± 1.4	3.12 ± 1.7	8.50 ± 5.6	6.48 ± 2.9

NO_2	**BR**	58.74 ± 73.7	29.40 ± 10	84.73 ± 62.6	59.27 ± 52.3	62.17 ± 51.5	116.39 ± 86.3	68.45 ± 29.3
	DR	43.50 ± 3.2	28.04 ± 14.5	42.10 ± 8.9	30.06 ± 5.7	41.63 ± 5.1	44.40 ± 5.8	38.34 ± 7.3
TSP	**BR**	211.1 ± 52.1		427.7 ± 287		411.8 ± 137		350.2 ± 121
	DR	165.3 ± 70		175.1 ± 51.7		246.7 ± 95		195.7 ± 44.4

BR= Before rain, DR= During rain, ∗($\mu g/m^3$)

Table 2 Daily averages of SO_2, NO_2 and TSP concentrations.

Date	Daily Average Concentration ($\mu g/m^3$)		
	SO_2	NO_2	TSP
10-7-99	16.06 ± 12.0	65.46 ± 64.1	-
11-7-99	6.29 ± 7.1	112.8 ± 50.0	553.1 ± 278
13-7-99	4.84 ± 1.6	109.6 ± 77.7	222.0 ± 68
15-7-99	11.30 ± 7.6	39.64 ± 38.3	342.3 ± 150
17-7-99	11.64 ± 8.4	23.73 ± 4.3	283.9 ± 129
20-7-99*	4.09 ± 1.3	43.33 ± 3.5	132.0 ± 41
22-7-99*	6.98 ± 6.0	32.06 ± 5.4	157.4 ± 16
24-7-99*	5.42 ± 6.0	36.40 ± 13.5	227.0 ± 113
26-7-99*	10.02 ± 7.2	42.20 ± 8.7	267.0 ± 27

* Subsequent rain of monsoon was observed

Table 3 National ambient air quality standards

Concentration in the ambient air ($\mu g/m^3$)				
Pollutant	Time weighed average	Sensitive area	Industrial area	Residential area
Sulphur dioxide	24 hours	30	120	80
Oxides of nitrogen as NO_2	24 hours	30	120	80
Total suspended particle	24 hours	100	500	200

Source: CPCB, 2000.

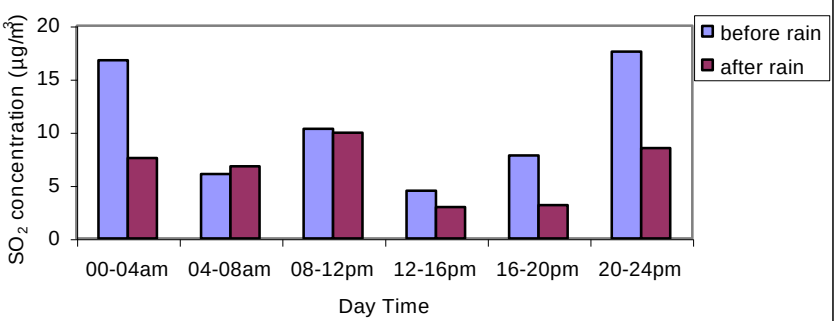

Figure-1: Comparison of SO_2 concentration before and during rainfall.

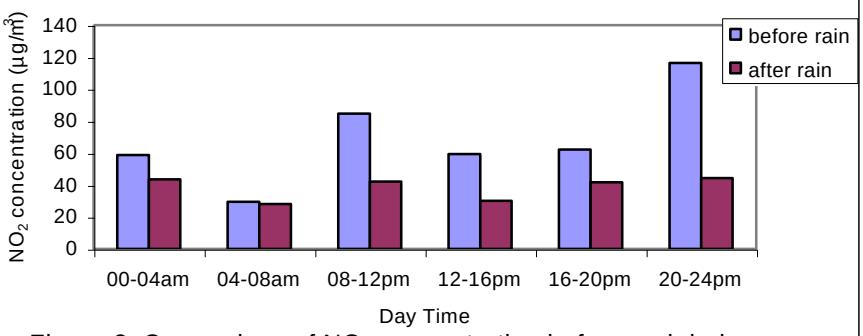

Figure-2: Comparison of NO_2 concentration before and during rainfall

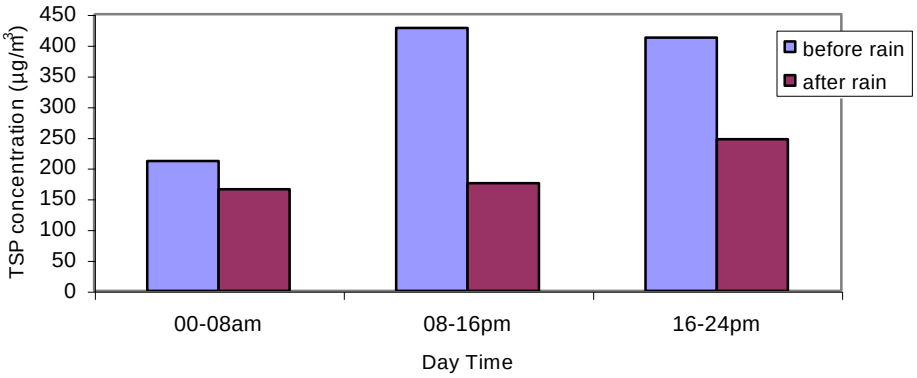

Figure-3: Comparision of TSP concentrtion before and during rainfall.

The linguistic quality is very modest.

We have improved the quality with my colleagues at the present workplace.

The same quantity changing designations are assigned e.g with suspended particulate matter it is not distinguished between SPM and TSP.

The experiments were done for Total Suspended Particles (TSP) and we replaced the TSP term consistently.

Values in PM10 and PM2.5 are quoted, while quantity is not used in the narrative at all.

The unrelated part of the has been deleted.

At least one reference made does not deal with the subject it is mention with.

I have checked the references again and only related references are used.

In introduction ozone stratospheric ozone is talked at high general level, but where turning to tropospheric ozone, with out any content they ask about different unrelated level aspects at another level.

The unrelated part has been deleted

On page no 5, a sophisticated mathematical formula describing the relation of SO_2 in air and SO_2 (sulphur of course is meant) together with considerations about drop size and sulphur content, but this

only quotation from other authors without any application to present paper.

We have rewritten that paragraph and the formula is omitted from the text.

Ozone once is abbreviated as O power 3 (O^3).
We have made this correction and also checked the manuscript for the other abbreviation used.

The metric system is not consistently used.
I have checked the manuscript and made the changes where it was necessary (i.e. LPM is changed in dm^3/min).