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Seasonal Trends and Correlation of Criteria Pollutants and Heavy Metals in Ambient Air of Bolpur (Semi Urban), India

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Abstract: Monitoring of particulate matter, gaseous pollutants and heavy metals has been done at Bolpur, a semi-urban area of West Bengal, India; during summer from April to June (2014) and winter from December to February (2015). In this study the elemental characterization of airborne particulate matter (PM₁₀) has been recognized as a significant air quality parameters with the study of criteria air pollutants like, PM, SO₂, NO₂, O₃, CO and Pb. In this study all pollutants were analyzed separately in both summer and winter seasons and were explained with the help of statistical techniques like ANOVA test, Pearson correlation test, box plot and cluster analysis. During this study period, variation of temperature, rainfall, wind speed and humidity were shown as one main factor for seasonal variation of air pollution. Seasonal variation of pollution levels in outdoor air of Bolpur was found to be highest at all the locations in the month of winter compared with summer. Three statistically significant cluster groups (Cluster-I, Cluster-II and Cluster-III) were displayed during Hierarchical Cluster Analysis depending on pollutants characteristics. **Keywords:** Particulate matter, Gaseous air pollutants, Heavy metals, Seasonal variation, Cluster analysis.

I. INTRODUCTION

In recent year's rapid growth of industrialization, urbanization, fossil fuel combustion and increasing economic growth are responsible for higher concentration of air borne particulate matter and gaseous air pollutants [1]. Particularly in developing countries like India, rapid industrialization and modernization activities led to the increased use of fossil fuels in huge amount for energy demand. In addition, India characterized by its rapid population growth, where 1.3 billion population also plays an important role in increasing environmental pollution [2]. It is of concern that atmospheric particulate pollution is one of the major pollutants that affect air quality in urban area and even rural areas is getting importance worldwide. Particulate matter is a complex mixture of solid and liquid particles that vary in size with aerodynamic diameters less than 2.5 mm and 10 mm (PM_{2.5} and PM₁₀) and contains heavy metals and ions and which remain suspended in ambient air. The major anthropogenic sources of particulate matter are the incomplete combustion of biofuel, fossil fuel burning, agricultural residual burning, municipal solid waste treatment, construction activities and emission from paved and unpaved roads [3]. Apart from the impact of particulate matter, gaseous air pollutants play significant roles on human health and environment. For example, the contribution and accumulation of many gaseous pollutants including SO₂, NO₂, O₃ and CO increase the pollution levels of atmosphere and susceptibility to respiratory diseases. Soluble components (e.g., metals and ionic compounds) and fine or ultrafine particulate matter may be absorbed through the respiratory tract surface into the systemic circulation. The aim of this paper is to examine the seasonal variation (summer and winter) of various air pollutants like total suspended particulate matter (TSPM), PM₁₀, PM_{2.5} and the harmful trace metals present in PM₁₀ samples collected during 2014-2015 from Bolpur, West Bengal.

II. MATERIAL AND METHODS

A. Study Area

Bolpur is a non-industrial and semi-urban area with a population of 80,210 people and area of 18 km². The metropolis has the geographic coordinate of 23°40'N 87°43' E. People of some areas in Bolpur mostly depend on wood or other solid biomass fuels for cooking and other purposes. Total six sites (Table 1 & Figure 1) from Bolpur were selected i.e., Station Chowrasta (S₁), Chitra More (S₂), Bolpur Post Office (S₃), Bolpur Bus Stand (S₄), Siksha Bhavana (S₅) and Sriniketan (S₆).

TABLE 1
Latitudinal and longitudinal locational details of sampling sites at Bolpur

Sampling sites	Latitude	Longitude
S ₁ Station Chowrasta	23°39'41"	87°41'47"
S ₂ Chitra More	23°40'04"	87°41'39"
S ₃ Post Office	23°39'48"	87°41'27"
S ₄ Bolpur Bus Stand	23°39'55"	87°40'53"
S ₅ Siksha Bhavana	23°40'52"	87°40'36"
S ₆ Sriniketan	23°39'56"	87°39'43"

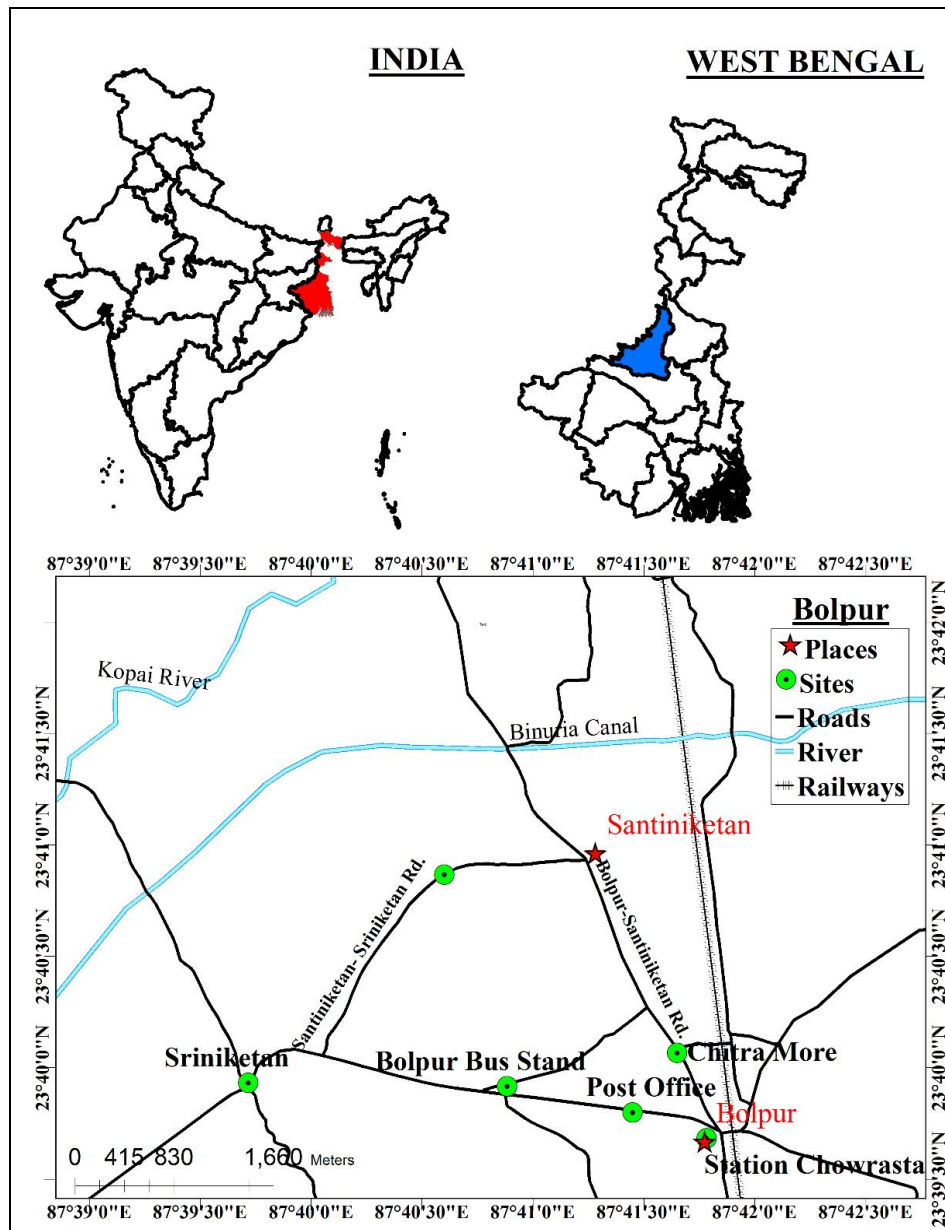


Figure 1: Map of the study area showing location of the sampling site and its surroundings places in Bolpur, India.

B. Sampling Method and Processing

- 1) **Particulate Matter (PM) Sampling:** Particulate matter samples were collected on glass fibre filter paper using Portable MiniVol TAS (Tactical Air Sampler) instruments (Air Metrics, Eugene, OR, USA) for size selective particulate matter i.e. TSPM, PM₁₀ and PM_{2.5}. The low flow technology of the instrument was developed with the association of U. S. Environmental Protection Agency (EPA). The particulate mass concentrations were measured gravimetrically by weighing the particles collected and knowing the total volume of air sampled. Filter papers were kept in a desiccator for 24 h before and after the sample collection. Field and laboratory blank filter samples were routinely analysed for particulate matter to evaluate analytical bias and precision.
- 2) **Sampling and Measurement of Gaseous Air Pollutants:** Sulphur di-oxide (SO₂), nitrogen dioxide (NO₂), ozone (O₃) and carbon monoxide (CO) data were collected using the portable gas sensor and different sensor head with data logger (AeroQual, Series-500). Before proceeding with the experiment, the air quality sensor was switched on. The sensor head was placed perpendicular to the air flow with the monitor and prepared for warm up. When the monitor is first switched on, it will warm up for 3 minutes. The reading will then flash for the next 7 minutes to indicate that the sensor is still in the warm up phase. It is recommended that the monitor is kept in Stand By mode when not being used to keep the sensor heated and prevent the build-up of contaminants.

C. Analysis of Heavy Metals

After gravimetric analysis, collected PM₁₀ sample filters were digested in mixed tri-acid i.e. HNO₃, HClO₄ and H₂SO₄ in the ratio of 5:1:1 using the method of Foley et al [4]. Reagent blank was also prepared by using unexposed filter paper following the same procedure. The digested solutions were then analyzed by using Anodic Stripping Voltameter (Metrohm 797 VA Computrace, Switzerland) for heavy metals like manganese (Mn), zinc (Zn), cadmium (Cd), lead (Pb), nickel (Ni), and cobalt (Co).

D. Statistical Analysis

One-way ANOVA was used to determine interrelationships between parameters and results are shown as the mean ± standard deviation (SD). Multiple DA (Discriminant Analysis) was performed to reveal and explain essential air quality parameters. DA is a dimension reduction statistical technique to classify data. Where necessary, results were transformed to meet the requirements of normality and equal variance.

E. Meteorological Data

Monthly meteorological parameters were recorded from six different sampling sites of Bolpur during study period. Continuous maximum and minimum temperature (°C), relative humidity (%), wind speed (m/s) and total precipitation were obtained from local weathering station. In summer the average temperature, relative humidity (RH), wind speed and total rainfall of Bolpur were 33.58 °C, 47.81%, 2.9 m/s and 332.92 mm. respectively whereas in winter the average temperature, relative humidity (RH), wind speed and total rainfall of Bolpur were 20.79 °C, 46.50 %, 2.61 m/s and 7.99 mm respectively (Figure 2).

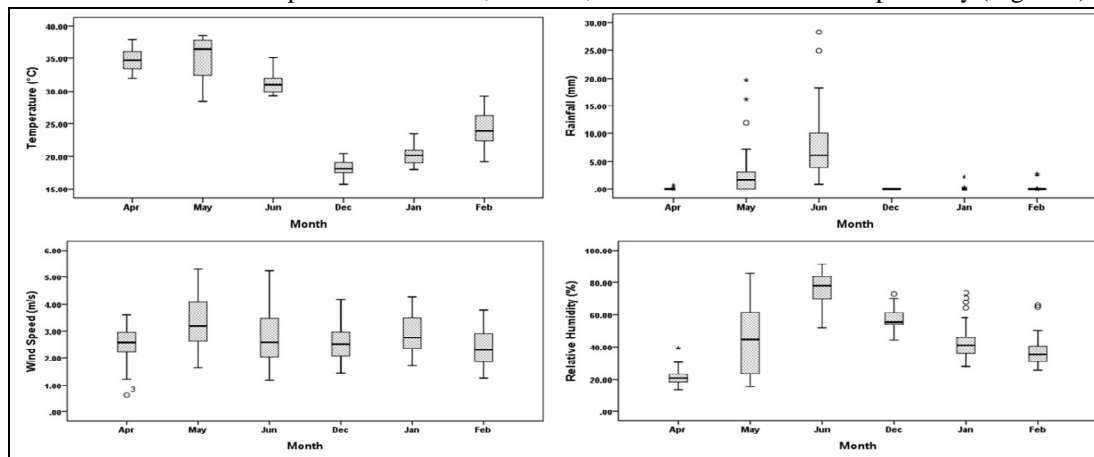


Figure 2: Monthly average temperature, total rainfall, wind speed and relative humidity in semi urban site (Bolpur)

III. RESULTS AND DISCUSSIONS

A. Comparative Study

Six criteria pollutants (carbon monoxide, lead, nitrogen dioxide, ozone, particulate matter, and sulphur dioxide) and other pollutants (heavy metals) were collected from Bolpur area in summer and winter seasons. These seasonal pollution data were analysed statistically in this study and described briefly.

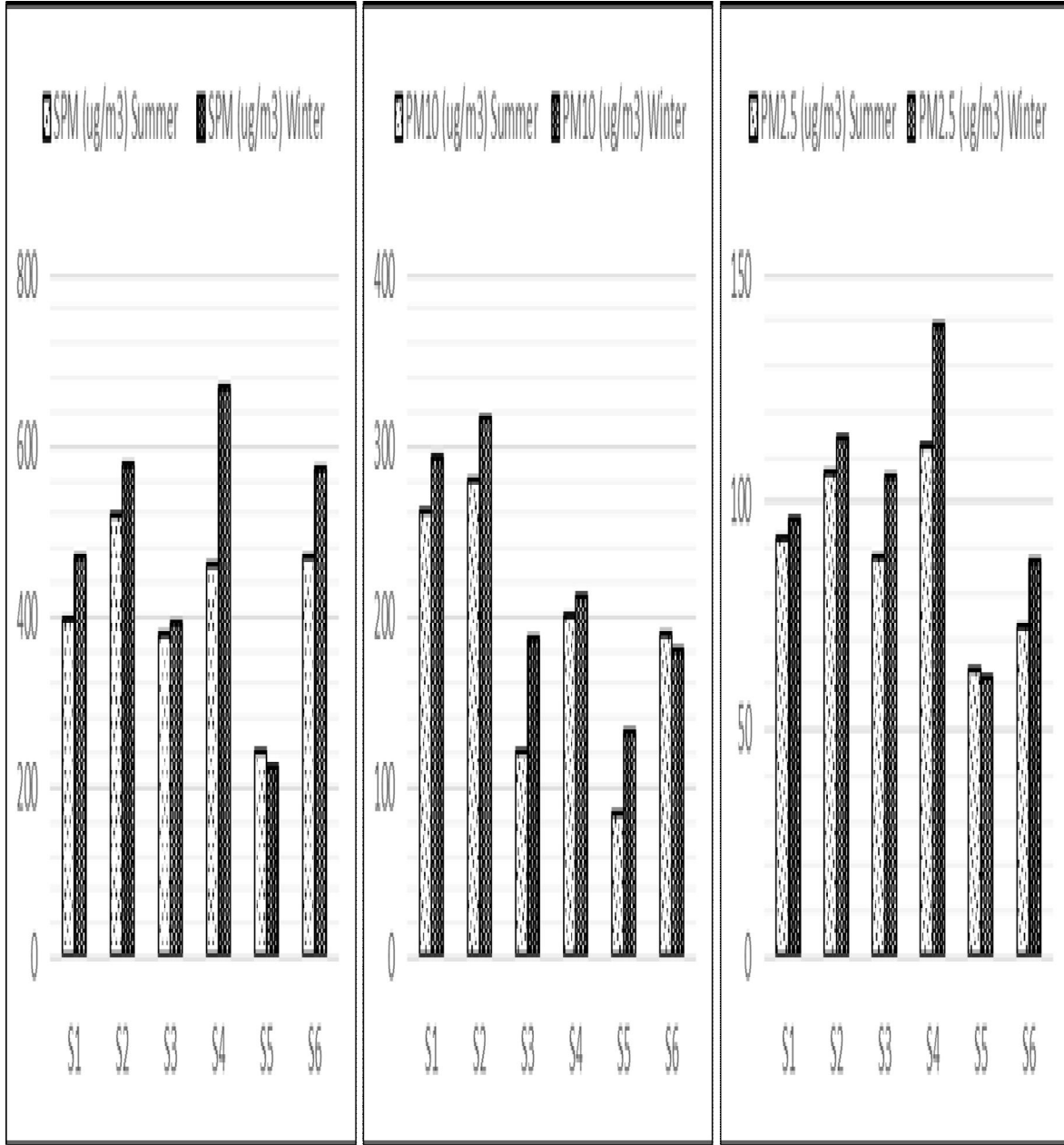


Figure 3: Seasonal variation of Particulate Matter in outdoor air of Bolpur.

In this study seasonal variation of TSPM, PM₁₀ and PM_{2.5} in outdoor air in six different sites of Bolpur are shown in Figure 3. Levels of TSPM in outdoor air sampling (24 hours) of Bolpur was varied from 242.23 µg/m³ to 519.3 µg/m³ in summer and 223.6 µg/m³ to 669.45 µg/m³ in winter, PM₁₀ was varied from 85.75 µg/m³ to 280.1 µg/m³ in summer and 133.34 µg/m³ to 315.25 µg/m³ in winter and PM_{2.5} was varied from 63.2 µg/m³ to 112.84 µg/m³ in summer and 61.67 µg/m³ to 139.04 µg/m³ in winter respectively. From the Figure 1, seasonal variation of particulate pollution levels shows that winter season had higher

pollution level than summer. In this study period S₅ (Siksha Bhavana) site had very low pollution level compared to the other sites in both season whereas the pollution level was high at S₄ (Bus Stand) site in winter season.

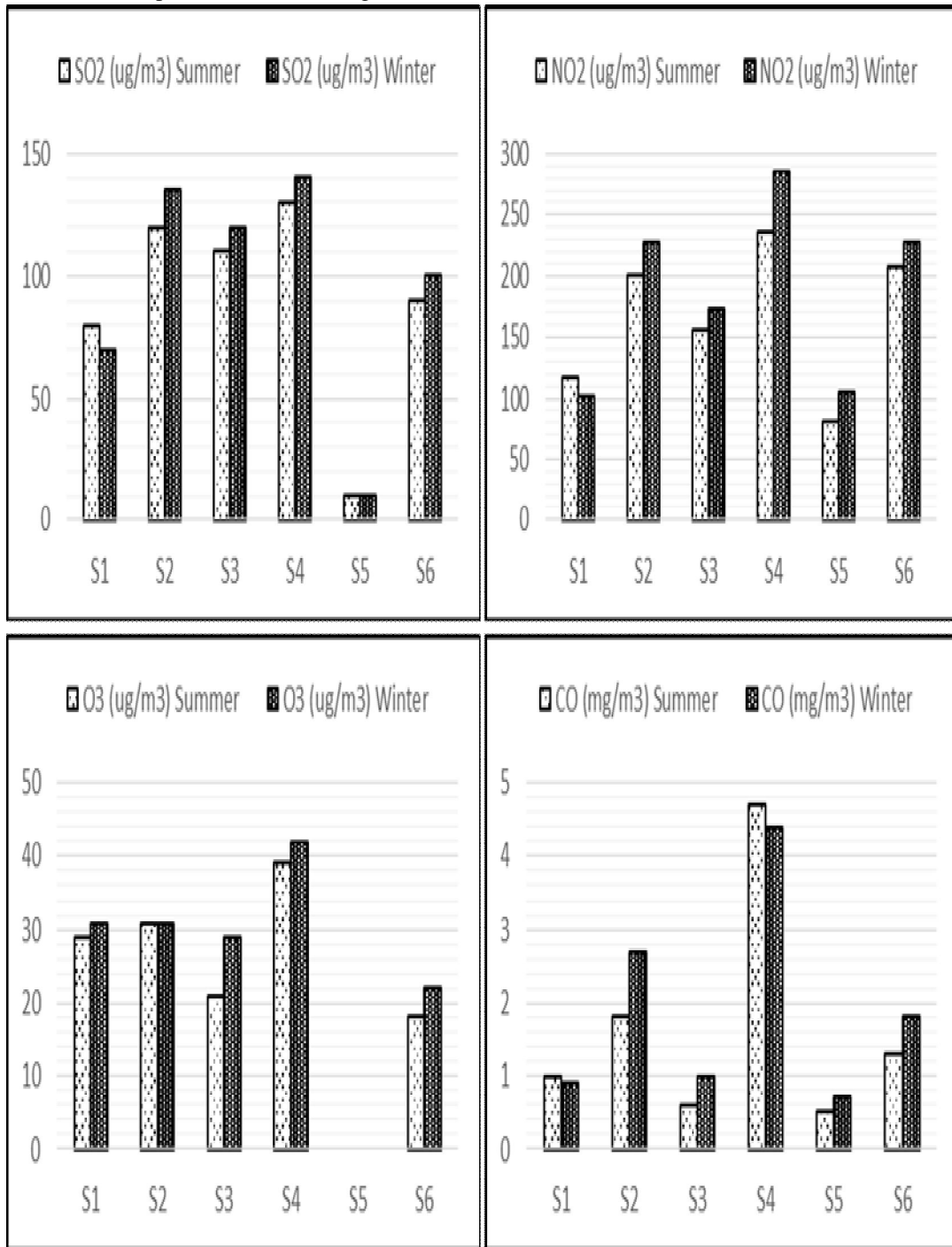


Figure 4: Seasonal variation of Gaseous Air Pollutants levels in outdoor air of Bolpur

The seasonal variation of ambient gaseous air pollution levels in outdoor air in six different sites of Bolpur are shown in Figure 4. Levels of SO₂ in outdoor air sampling of Bolpur varied from 10 µg/m³ to 130 µg/m³ in summer and 10 µg/m³ to 140 µg/m³ in winter, NO₂ varied from 82 µg/m³ to 237 µg/m³ in summer and 105 µg/m³ to 285 µg/m³ in winter, O₃ varied from 0 µg/m³ to 39 µg/m³ in summer and 0 µg/m³ to 42 µg/m³ in winter and CO varied from 0.5 mg/m³ to 4.7 mg/m³ summer and 0.7 mg/m³ to 4.3 mg/m³ summer respectively. In this study, at S₅ (Siksha Bhavana) site ozone concentration were observed in zero level during

the summer and winter season. Sulphur di-oxide, NO₂ and O₃ levels in all sites except S₄ site were very high which exceeded the NAAQS. Higher levels of CO were found at S₂ and S₄ sites due to high vehicular activities.

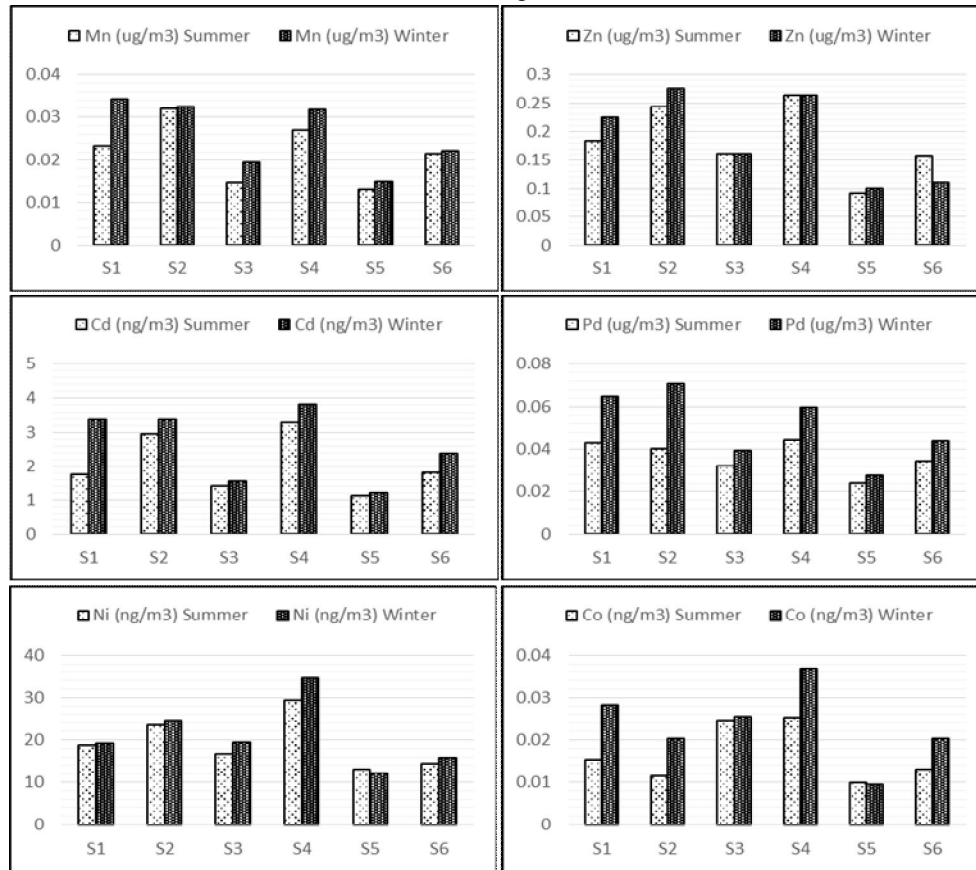


Figure 5: Seasonal variation of heavy metal concentration levels in outdoor air of Bolpur

Figure 5 show that, concentration of manganese (Mn), zinc (Zn), cadmium (Cd), lead (Pb), nickel (Ni), and cobalt (Co) in PM₁₀ samples were found in the range of 0.013-0.032 µg/m³, 0.092-0.263 µg/m³, 1.148-3.302 ng/m³, 0.024-0.044 µg/m³, 12.948-29.297 ng/m³ and 0.01-0.025 ng/m³ respectively during summer and the same for winter were 0.015-0.034 µg/m³, 0.101-0.276 µg/m³, 1.2063-3.833 ng/m³, 0.0278-0.071 µg/m³, 12.083-34.688 ng/m³, 0.009-0.0367 ng/m³ respectively. Levels of heavy metals were found highest at all the locations in the month of winter compared to summer. Generally the winter season is characterized by low wind speed and serenity as compared to the summer season. High concentration of heavy metals may be because of poor dispersing condition due to low wind speed and surrounding conditions in this time.

TABLE 2

Annual Mean ± SD concentration of Particulate matter, gaseous pollutants and heavy metals in Bolpur

Parameters	S1	S2	S3	S4	S5	S6
TSPM (µg/m ³)	431.41 ± 50.50	549.8 ± 43.13	385.93 ± 10.79	564.15 ± 148.84	232.91 ± 13.17	520.24 ± 74.77
PM ₁₀ (µg/m ³)	277.75 ± 22.74	297.67 ± 24.85	153.23 ± 46.33	206.01 ± 7.21	109.54 ± 33.65	184.38 ± 5.91
PM _{2.5} (µg/m ³)	94.68 ± 2.91	110.74 ± 5.71	97.03 ± 12.79	125.97 ± 18.49	62.44 ± 1.08	79.83 ± 9.85
SO ₂ (µg/m ³)	75 ± 7.07	127.5 ± 10.6	115 ± 7.07	135 ± 7.07	10 ± 0	95 ± 7.07
NO ₂ (µg/m ³)	109 ± 11.31	214 ± 18.38	164.5 ± 12.02	261 ± 33.94	93.5 ± 16.26	217 ± 14.14
O ₃ (µg/m ³)	30 ± 1.41	31 ± 0	25 ± 5.65	40.5 ± 2.12	0	20 ± 2.83

CO ($\mu\text{g}/\text{m}^3$)	0.95 ± 0.07	2.25 ± 0.63	0.8 ± 0.28	4.55 ± 0.21	0.6 ± 0.14	1.55 ± 0.35
Mn ($\mu\text{g}/\text{m}^3$)	0.028 ± 0.007	0.032 ± 0	0.017 ± 0.003	0.029 ± 0.003	0.014 ± 0.001	0.021 ± 0.001
Zn ($\mu\text{g}/\text{m}^3$)	0.204 ± 0.028	0.259 ± 0.023	0.161 ± 0	0.263 ± 0.001	0.096 ± 0.006	0.134 ± 0.03
Cd (ng/m^3)	2.571 ± 1.151	3.169 ± 0.305	1.483 ± 0.104	3.567 ± 0.376	1.177 ± 0.041	2.104 ± 0.398
Pb ($\mu\text{g}/\text{m}^3$)	0.054 ± 0.015	0.055 ± 0.021	0.035 ± 0.005	0.052 ± 0.01	0.025 ± 0.002	0.039 ± 0.006
Ni (ng/m^3)	19.029 ± 0.342	24.062 ± 0.883	18.086 ± 1.97	31.992 ± 3.812	12.516 ± 0.611	15.154 ± 0.917
Co (ng/m^3)	0.021 ± 0.009	0.015 ± 0.006	0.025 ± 0.001	0.031 ± 0.008	0.009 ± 0	0.016 ± 0.005

TABLE 3
Pearson correlation of different air pollutants of Bolpur area

	TSPM	PM10	PM2.5	SO2	NO2	O3	CO	Mn	Zn	Cd	Pb	Ni	Co
TSPM	1	0.672	0.779	.870*	.872*	.845*	0.729	.819*	0.776	.863*	0.795	0.727	0.523
PM ₁₀		1	0.592	0.52	0.267	0.688	0.288	.928**	0.779	0.754	.938**	0.488	0.2
PM _{2.5}			1	.885*	0.717	.950**	0.804	0.773	.949**	.866*	0.804	.958**	0.798
SO ₂				1	.838*	.891*	0.653	0.643	0.782	0.708	0.678	0.763	0.717
NO ₂					1	0.675	.834*	0.519	0.611	0.7	0.467	0.728	0.529
O ₃						1	0.708	.820*	.906*	.859*	.875*	.866*	.826*
CO							1	0.619	0.746	.844*	0.563	.922**	0.628
Mn								1	.912*	.943**	.983**	0.743	0.39
Zn									1	.936**	.919**	.918**	0.61
Cd										1	.909*	.896*	0.536
Pb											1	0.739	0.49
Ni												1	0.749
Co													1

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

The annual average (mean ± SD) concentration of pollution level in ambient air of Bolpur is shown in table 2. During the study periods, there are significant variations noticed in the mass concentration of TSPM, PM₁₀ and PM_{2.5} in various sites which are summarized in Table 2. Average concentration of each site was compared with the national ambient air quality standard (NAAQS, 2009) and found that all particulate matters concentrations were above the National Ambient Air Quality Standard (NAAQS, 2009) levels prescribed by CPCB, India (Table 2).

The proximity sources of PM were roadways near the sampling point, the influence of traffic-induced coarse dust from roadside, vehicular traffic, fossil fuel combustion, which makes difference between these sites. Resuspension is due to the high temperature and wind velocity as a result the ratios of TSPM, PM_{2.5} and PM₁₀ shifts to the lower values during the summer months [5]. This is plausible because mechanically produced particles, and in particular resuspension, depend not only on the vehicle frequency but also on the condition of the roadway (e.g., clean/dirty, wet/dry) [6]. Concentrations in winter were consistently higher compared to summer and this can be due to the differences in meteorological parameters as well as variations in source strengths. Significant differences between PM concentrations in summer and winter have been recorded in various pollution studies [7, 8, 9], and higher winter concentrations are attributed to larger combustion source strength in the winter combined with calm weather conditions and a shallow boundary layer which affects pollutant dispersion adversely [10]. Sulphur dioxide (SO₂) emitted during fossil fuel combustion, is a major precursor of new airborne particles. Vehicle pollutants believed to cause adverse health impacts include diesel particulate matter (DPM), which include ultrafine particles; criteria pollutants, such as, NO₂ and carbon monoxide; and organic compounds such as benzene and butadiene [11]. Vehicular emissions, automobile lubricants, wear and tear of tyres and construction activities are the possible sources of Cd in ambient air. Various products like batteries, toys, etc. contains Cd and is more common in household garbage which are other sources of Cd

[12]. The contribution of Zn and Mn in this study may be the earth crust or wind blow soil and vehicular emission as a contributor in PM₁₀ [13]. In ambient air Co may originate mainly from coal burning and re-suspension of upper soil layer [14]. Lead is a major constituent of the lead-acid battery used extensively in car batteries [15]. In vehicular emissions CO, oxides of nitrogen (NO_x), sulphur dioxide (SO₂), Pb and particulates are the main pollutants find out in the investigators analysis of diurnal and seasonal variations study by Mondal et al [16] and Pandey et al [17].

B. Agglomerative Hierarchical Cluster Analysis

Agglomerative Hierarchical Cluster Analysis was used to find out the similarity among the sampling sites in Bolpur area. The results of agglomerative hierarchical cluster analysis (AHCA) performed on the dataset after standardization is displayed as dendrogram in Figure 6. The clustering pattern in figure shows three statistically significant groups namely, Cluster-I, Cluster-II and Cluster-III from six sampling sites according to spatial resemblance. Cluster-I included sampling sites S₄, S₂ and S₆; Cluster-II includes sampling sites S₃ and S₁; and Cluster-III included sampling site S₅. These grouping among the sampling sites clearly identify the characteristic of ambient air quality and its sources. Sampling sites S₄, S₂ and S₆ are the main market area where population density is very high; sampling sites S₃ and S₁ are well known for high traffic density and vehicular emission throughout the day; and sampling site S₅ is indicating the silent zone where population and traffic density is low.

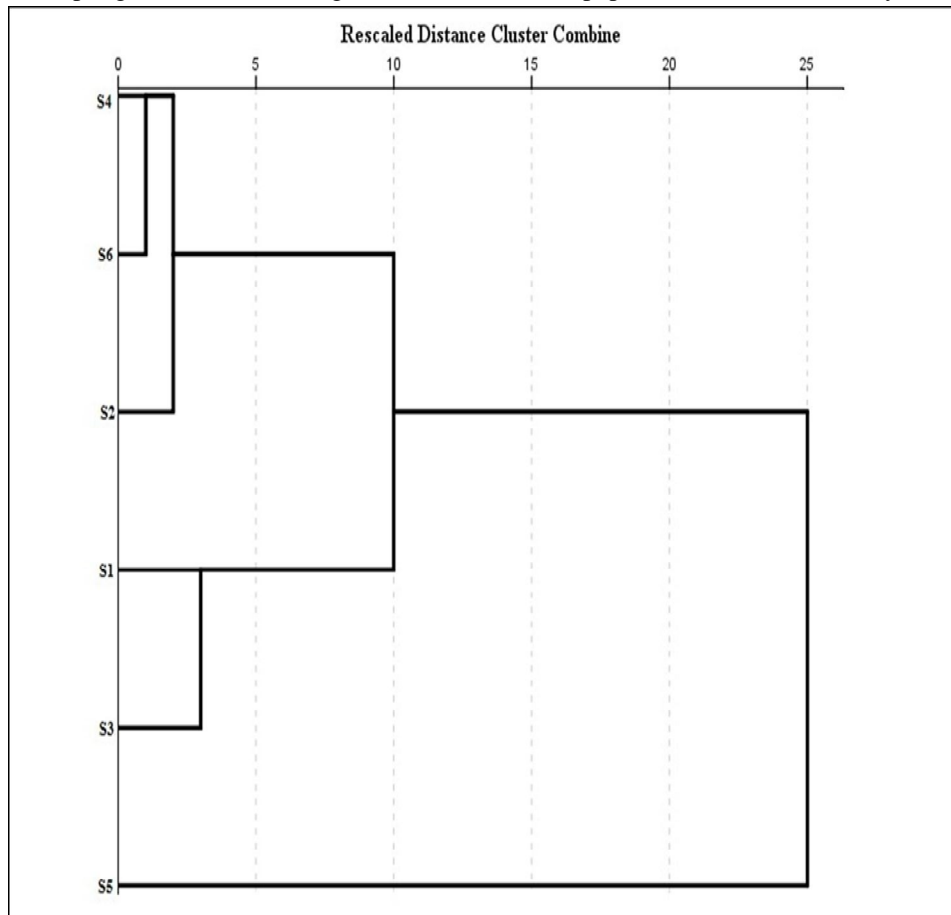


Figure 6: Dendrogram of multivariate cluster statistical analysis exhibiting three differentiated groups

IV. CONCLUSIONS

The variations of ambient levels of Particulate matter (TSPM, PM₁₀ and PM_{2.5}), gaseous air pollutants (SO₂, NO₂, CO and O₃) and heavy metals (Mn, Zn Cd, Pb, Ni and Co) were analysed at the semi urban area of Bolpur during April 2014 to February 2015. Emission from anthropogenic activities mainly traffic, automobile vehicles and biomass burning are the major local

outdoor sources of pollutants in the absence of industrial activities. These pollutants were found to have variation in accordance to variation of meteorological parameter during this study period. During winter season particulate matter levels were high due to temperature inversion, high humidity, low rainfall and low wind speed which help particles to settle down. For that reason the metal concentration also showed variation in semi urban area. Depending on behavioural characteristic of sites, there are three clusters (I, II and III) which were extracted by statistical analysis which will help to monitor the ambient air quality in Bolpur.

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