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Chemical characterization of PM₁ around an Industrial area

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Abstract

PM₁ (particles less than 1 μm in diameter) were collected continuously from October to November 2010. The concentrations of water-soluble ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, NO₃⁻ and SO₄²⁻) and metals (Cr, Ni, Cu, Fe, Mg, Mn, Pb, Zn) were determined in the filter samples to characterize the chemical composition of PM₁ over Nagpur, India at an industrial area during winter. The mean PM₁ mass concentration was 53.3 μg/m³. Water-soluble inorganic ions were dominant chemical species and occupied to 32.5% of PM₁ mass. NH₄⁺, SO₄²⁻ and NO₃⁻ were the major species of ionic compounds, which accounted for 88.6% of total ions concentration. Metals occupied 7.8 % of PM₁ mass. Principle component analysis indicates that secondary sources, industrial emissions and re-suspension of road dust are the sources of PM₁. The aim of this study is to evaluate PM₁ pollution at industrial area in Nagpur city, India and find the sources of PM₁. For the effective management of the air quality, it is very important to identify the sources of PM₁. Chemical analysis of PM₁ could provide information on the presence of chemical species that could contribute to particle toxicity. Inhalation exposure to PM₁ is concern for both environmental and occupational health research.

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INTRODUCTION

Atmospheric aerosols are currently a subject of high scientific and political interest, which is due to their important effects on climate, human health, ecosystems and agricultural yields as well as visibility [1]. In the last few years, a large interest for aerosol fine particles has increased within the research community. There is a consensus that PM_{2.5} (fine) and PM₁ (sub-micron) particles would be the more suitable size than PM₁₀ for health related aerosol study [2]. Both PM_{2.5} and PM_{1.0} could enter the gas-exchange regions of the lungs, and much smaller particles (<100 nm) may pass through the lungs to affect other organs [3]. Thus determining their composition is essential to understanding their properties and reactivity and their environmental effects [4]. Most anthropogenic pollution sources are combustion-related and generate particles with diameters < 1 μm [5]. PM₁ can travel for days over distances of several hundred kilometers from the source [6]. The environmental and health impacts of PM₁ are significant. Data on levels and speciation of PM₁ in all

over the world are very scarce. The aim of this study is to evaluate PM₁ pollution at industrial area in Nagpur city, India and find the sources of PM₁. Nagpur lies precisely in the center of the India with the [zero mile](#) marker indicating the geographical center of India. It is the largest city in central India having a population of 4,653,171 (census of India, 2011) and with the area of approximately 220 km² (latitude 21°06' N, longitude 79°03' E). Nagpur is situated at a height of 312.42 meters above sea level. It has continental type of climate with three distinct seasons: summer, monsoon, and winter. The climate of Nagpur city is characterized by an extremely hot summer and a cold winter. The city experiences tropical climate and record the rise of temperature up to 48 °C in summer season (March to May). The cold season is from November to February where the temperature drops down to as low as 6°C to 8°C. Hingana is the industrial area in Nagpur; sampling was carried out in this area, which is surrounded by rolling mills and electronic zone.

MATERIALS AND METHOD

PM₁ samples were collected from October to November 2010 using a low volume Federal Reference Method Sampler (Partisol Model 2000, Rupprecht & Patashnick Co., Inc., US EPA) operating at a flow rate of 16.7 l min⁻¹ for a 24 hourly duration. The sampler was placed on the roof of building from the surface of 9 m high building. Sampling was carried out in Industrial area. The samples were collected on Whatman PTFE (Teflon) filters of 47mm diameter and 2µm pore size, for metals and ion analysis. During sampling, field blank filters were collected to reduce gravimetric bias due to filter handling during or after sampling. The filters were weighted by using a high-precision five-digit electronic balance (Mettler AE 163). Each filter paper used for sampling was pre-conditioned and post conditioned at 40 ± 3% relative humidity and in controlled environment at 25°C for over 24 hour before and after sampling.

Water Soluble Inorganic Ion Analysis

The concentrations of four anions (F⁻, Cl⁻, NO₃⁻, SO₄²⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) were determined in aqueous extracts of the filters prepared in three steps using ultra-pure water. The Teflon filter was placed in a vial with 25 ml of ultra-pure water and sonicated for 60 min. The extracted solution was then shaken for 12 hours and filtered through a syringe filter and stored at 4 °C until further analysis.

Analysis of samples for concentration of anions was performed using (Make: Dionex Model: ICS 3000, Germany) ion chromatograph equipped with Dionex Ionpac AG11-HC guard column and AS11-HC separation columns, 25 µL sample loop and conductivity detector. A 30 mM KOH was used as an eluent at a flow-rate of 1.0 mL min⁻¹. For analysis of cations in selective samples, the same system was used in combination with AG5 and AS5 cation exchange guard and separation column, respectively. A 6 mM methanesulfonic acid was used as an eluent for cation analysis. The limits of detection for cations and anions were 1 ppb in Dionex ion chromatograph. Dionex five anions standard and Dionex five cations standard were used for the calibration of the ion chromatograph for determination of anions and cations respectively.

Metal Analysis

Samples for PM₁ was collected on teflon filter paper used to determine the toxic metals which includes Cr, Ni, Cu, Fe, Mg, Mn, Pb, Zn, and Cd by inductively coupled plasma optical emission spectrometry, (model-optima 4100 DV, Perkin Elmer, USA). Blank test background contamination was monitored by using operational blanks (unexposed filter) which were processed simultaneously with field samples. Blanks

were cleaned and prepared with the same procedures applied to the actual samples. The filter paper was digested with concentrated nitric acid (Merck) in a Teflon vessel in a microwave digestion chamber (ETHOS make-milestone, Italy). The sample was digested for twenty minutes and then filtered through Whatman 42 (Ashless filter papers 125mm) filters into a properly cleaned volumetric flask. Samples are analyzed by spiking with a known amount of metals to calculate recovery efficiencies.

RESULTS

The average concentration for PM₁ was 53.3 ± 23.9 µg/m³. The 24-hourly PM₁ concentration varied from 21.9 to 102 µg/m³. **Table 1.** Shows average mass concentration of PM₁. There is no ambient air quality standards for PM₁ but several epidemiological studies suggested that PM₁ can easily penetrate in the alveolar region of lungs. It is a matter of serious health concern.

Table 1. Average mass concentration and associated Standard deviation of PM₁, water soluble ions and metals in (µg/m³).

Species	Concentration (µg/m ³)			
	Avg ^a	Std ^b	Min ^c	Maxi ^d
PM ₁	53.30	23.90	21.90	102.00
NH ₄ ⁺	5.80	2.95	2.37	10.73
K ⁺	0.37	0.23	0.13	0.77
Mg ²⁺	0.36	0.24	0.10	0.79
Ca ²⁺	1.13	0.49	0.39	2.17
SO ₄ ²⁻	7.91	4.21	3.74	16.54
NO ₃ ⁻	1.66	1.29	0.36	4.02
Zn	1.01	0.35	0.26	1.38
Ni	0.34	0.06	0.26	0.46
Pb	0.53	0.15	0.05	0.65
Cu	0.32	0.09	0.03	0.39
Mn	0.21	0.21	0.01	0.66
Fe	1.71	0.73	0.68	2.79
Cr	0.04	0.02	0.01	0.07

^aAverage, ^bStandard deviation, ^cMinimum, ^dMaximum

The concentrations of metals were in the following order of magnitude: Fe > Zn > Pb > Ni > Cu > Mn and Cr. Metals contributed up to 7.8% of the PM₁ mass. The trend for water-soluble inorganic ions were NH₄⁺, SO₄²⁻, NO₃⁻, Ca²⁺, K⁺, Mg²⁺. Water-soluble inorganic ions were dominant chemical species and occupied

32.5% of PM₁ mass. NH₄⁺, SO₄²⁻ and NO₃⁻ were the major species of ionic compounds, which accounted for 88.6% of total ions concentration.

Source Apportionment of PM₁

Principle component analysis.

Principal component analysis (PCA) was used for the identification and evaluation of the contributions of the main emission sources at the industrial area. PCA was performed by the Varimax Rotated Factor Matrix method, based on the orthogonal rotation criterion which maximizes the variance of the squared elements in the column of a factor matrix, using a statistical package SPSS. SPSS extracted three factors associated with eigen values > 1 which are shown in Table 2. The greater the loading of a variable the more that variable contributes to the variation accounted for the particular Factor or Principal Component (PC).

Table 2. Rotated Component Matrix

Species	Component		
	1	2	3
Ca			0.791
Cu		0.927	
Fe		0.675	
K			
Mg			0.723
Mn			0.779
NH ₄ ⁺	0.507		
Ni		0.850	
NO ₃ ⁻	0.744		
Pb		0.863	
SO ₄ ²⁻	0.824		
Zn		0.852	

Factor 1: This had loadings for SO₄²⁻, NO₃⁻ and NH₄⁺, which explained 28% of the total variance. It represents the secondary formation of ammonium sulfate, ammonium nitrate in the atmosphere.

Factor 2: It shows high loadings on Cu, Pb, Ni, Zn and Fe which explained 27.68% of the total variance. The possible sources may be industrial emissions from iron and steel industry or ferrous smelters. Ni could be derived from fuel oil combustion as well as industrial combustion. Coal and oil combustion facilities produce fine particles in the sub-micron size range enriched by heavy metals [7].

Factor 3: This is loaded with Ca, k, and Mg, which explained 20.6 % of the total variance referring to soil and road side dust. These elements are mainly of natural origin

Table 3. % Variance explained by extracted factors

Rotation Sum of Squared Loading		
Total	% of Variance	Cumulative %
3.366	28.050	28.050
3.322	27.686	55.736
2.480	20.663	76.399

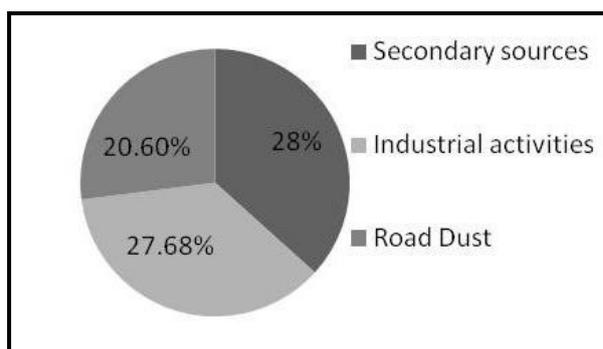


Fig 1. % Contribution of different sources in overall PM₁ mass

DISCUSSION

Since the sampling was carried out in winter; lower temperature, low wind speed, lower mixing height and poor dispersion conditions were responsible for transformation of anions from gas phase to particle phase. Ammonium sulfate is the most stable while ammonium chloride is the most volatile, hence ammonia prefers to react with sulfuric acid or sulfate [8]. From previous studies it can also be said that most of the fine particulate SO₄²⁻ and NO₃⁻ exist as ammonium nitrate (NH₄NO₃) and ammonium sulfate [(NH₄)₂SO₄] [9]. Other studies carried out in India and China also reveals that water-soluble inorganic ions were dominant chemical species contributing to PM₁ mass [9, 10, 11]. Regarding metals, high-temperature processes such as metal smelting and fuel combustion are usually the source of non-crustal volatile metals (e.g. Cd, Zn, Pb) in the atmosphere [12]. Fe was found to be significant in this study. Fe can also have a strong anthropogenic origin due to the large metallurgical industries. Chronic exposure to Fe can cause benign Pneumonia-conuisis and can enhance harmful effects of SO₂ and various carcinogens. Ingestion of Fe in excessive quantity inhibits the activity of many vital enzymes [13]. Comparing other studies on source apportionment of PM₁, the identified sources are mostly anthropogenic. Vehicle exhaust, secondary aerosols, waste incinerator/biomass burning, coal combustion. [9, 10, 14].

CONCLUSIONS

In this study, we investigated the concentration level of PM₁ in the industrial atmosphere of Nagpur City, India. The 24-hourly PM₁ concentration varied from 21.9 to 102 µg/m³ with an average of 53.3 µg/m³. Sulfate and nitrate were the major components seen in PM₁. Most of the metals like Ni, Cr, Pb, Zn are harmful for humans and can cause serious health concerns and as they are associated with PM₁ they can be easily inhaled and retained in our respiratory system for longer duration making more serious concerns. Source apportionment by PCA produced three factors indicating that secondary sources, industrial combustion, and re-suspension of the road dust were the main sources for PM₁. Further studies are required on polycyclic aromatic hydrocarbons and water soluble organic component as these are associated with mostly a sub-micron fraction.

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