

# CHEMICAL SPECIATION OF PARTICULATE MATTER POLLUTION IN URBAN DHAKA CITY

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## ABSTRACT

Dhaka, the capital and largest city of Bangladesh, lacks a regular air pollution monitoring network to measure and assess ambient air pollution level. Several academic and research projects attempted to measure a limited number of air pollutants near roadways in the central business district. These studies revealed that ambient concentrations of lead, benzene, particulate matter, carbon monoxide, oxides of sulfur, and nitrogen in the air of Dhaka have exceeded health based standards set by both the World Health Organization (WHO) and United States Environmental Protection Agency (US EPA). The measured peak concentrations for some pollutants were found to be several folds higher than the international standards. In one instance, a study conducted by the Bangladesh Atomic Energy Commission showed that Dhaka's ambient lead level was highest in the world for a part of the year 1996.

With the assistance of World Bank, Bangladesh Department of Environment (DOE) recently began an air quality management project in the Dhaka City. An international consultant helped the DOE personnel to setup an air-monitoring network in selected locations of Dhaka City to collect and measure particulate emissions. This paper presents results of the chemical analysis conducted on the ambient filters collected by the World Bank and DOE monitoring effort. Due to financial constraint, the World Bank and DOE limited their objective to only measurement of the level of ambient particulate concentrations. However, without a detailed chemical speciation of the collected filter, it is not possible to identify pollution sources and their relative contributions.

Furthermore, in order to understand public health implications and assess exposure risks, chemical components of the particulate pollution must be known. In a joint effort, the Bangladesh Environment Network (BEN) and the international consultant for the Dhaka air quality management project arranged for the laboratory analysis of the collected filters. The world renowned Desert Research Institute (DRI), Reno, Nevada, conducted chemical analysis of the filters. Dr. Judith Chow of DRI, who pioneered many chemical techniques for analysis of particulate pollution, graciously offered the service to analyze these filters at no cost.

Among the sampling sites, the Farmgate site has shown the maximum ambient level, as high as 526 microgram of  $PM_{2.5}$  per cubic meter of air volume. This level is more than eight folds higher than the US EPA standard of 65 microgram per cubic meter. The fine  $PM_{2.5}$  size pollutants are primarily emitted by combustion processes and automobile emissions. As Farmgate is considered one of the most congested traffic intersections in Dhaka, such an extremely high  $PM_{2.5}$  level is the direct result of vehicular emissions.

The chemical analysis of the filters at DRI laboratory identified presence of the following chemical species in the Dhaka's particulate air pollution: elements of sodium (Na) to lead (Pb), chloride (Cl), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), ammonium ( $\text{NH}_4^+$ ), organic carbon (OC), elemental carbon (EC), etc. Very high concentrations of sulfate, organic carbon, lead, nitrate, etc. suggest that particulate emissions are predominately formed by the combustion products of dirty fuels (i.e., high sulfur diesel and leaded petrol) used in automotive engines.

## **Nature and Sources of the Particulate Matter Pollutant**

Particulate matter (PM) is the general term used for a mixture of solid particles and liquid droplets found in the ambient air. Some particles are large or dark enough to be seen as soot or smoke. Others are so small that they can be detected only with an electron microscope. These particles, which come in a wide range of sizes ("fine" particles are less than 2.5 micrometers in diameter and coarser size particles are larger than 2.5 micrometers), originate from many different stationary and mobile sources as well as from natural sources. Fine particles ( $\text{PM}_{2.5}$ ) result from fuel combustion from motor vehicles, power generation, and industrial facilities, as well as from residential fire-places and wood stoves. Coarse particles ( $\text{PM}_{10}$ ) are generally emitted from sources, such as, vehicles travelling on unpaved roads, materials handling, and crushing and grinding operations, as well as windblown dust. Some particles are emitted directly from their sources, such as smokestacks and cars. In other cases, gases such as sulfur oxides,  $\text{SO}_2$ ,  $\text{NO}_x$ , and VOC interact with other compounds in the air to form fine particles, which are called secondary particulate matters. Their chemical and physical compositions vary depending on location, time of year, and weather.

## **Health and Environmental Impacts**

Inhalable PM includes both fine and coarse particles. These particles can accumulate in the respiratory system and are associated with numerous health effects. Exposure to coarse particles is primarily associated with the aggravation of respiratory conditions, such as asthma. Fine particles are most closely associated with such health impacts as increased hospital admissions and emergency room visits for heart and lung disease, increased respiratory symptoms and disease, decreased lung function, and even premature death. Sensitive groups that appear to be at great risks to such effects include the elderly, individuals with cardiopulmonary disease, such as asthma in children. In addition to health problems, PM is major cause of reduced visibility and increased haze in many parts of the world. Airborne particles also can cause damage to paints and building materials.

## **Sampling Location and Methodology**

Bangladesh DOE has measured ambient levels of suspended particulate matters in Dhaka in the past few years but few measurements of  $\text{PM}_{10}$  or  $\text{PM}_{2.5}$  have been taken by the agency. During the period of August 3 to October 3, 1998, DOE used Airmetrics Minivol Portable Samplers to measure  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  concentrations at three locations

in Dhaka. These locations included the roof of the DOE office building, the roof of World Bank office in central Dhaka, and at street level near the police box in the Farmgate intersection of the city. Most samples were taken over six hour periods during mid-day when weather conditions were mostly windy, rainy, and cloudy. Two samplers were run concurrently: one equipped with a quartz fiber filter to be used for carbon analysis and the other with a stretched Teflon filter to be used for elemental analysis.

The patented low-flow technology featured in Airmetrics Minivol Portable sampler was jointly developed by the US EPA and Lane Regional Air Pollution Authority, Oregon, USA to address the need for portable survey sampling. The US EPA owns nearly 200 Minivol samplers, which are housed at East and West Coast repositories for agency use. Compact, lightweight, and battery-operated, the minivol sampler is ideal for sampling at remote locations, at sites where no permanent monitoring site exists, or at areas without electrical power.

The Airmetrics Minivol Portable Sampler is basically a pump with a programmable timer which can be set to make up to 6 sampling "runs" within a 24 hour period. The timer can start and stop the pump at pre-set times over a 7 day period. The pump draws air through a particle size separator and then through a filter medium. The 10-micron or 2.5 micron particle separation is achieved by impaction. The particulate sample can be caught on any standard 47mm filter medium, which enables gravimetric or chemical analysis. Inside the sampler, air is pulled through the inlet tube (downstream from the filter) to the twin cylinder diaphragm pump. From the pump, air is forced through a standard flow meter, where it is exhausted to the atmosphere inside the sampler body. The flow meter is used to indicate and adjust the flow rate.

## Sampling Results

A total of 41 filter sets were collected during the sampling period. Table 1 summarizes results obtained from the quartz fiber filters.

**Table 1: Summary of particulate concentrations in microgram/cubic meter**

Site	PM Size Fraction	No. of Samples	Minimum	Maximum	US EPA Standard
Farmgate	PM <sub>10</sub>	2	346	510	150
Farmgate	PM <sub>2.5</sub>	5	356	526	65
DOE	PM <sub>10</sub>	13	59	178	150
DOE	PM <sub>2.5</sub>	5	28	181	65
World Bank	PM <sub>10</sub>	16	126	207	150

Concurrent suspended particulate matter samples of two cut size PM<sub>10</sub> and PM<sub>2.5</sub> were taken on September 30, October 1, and October 3. The PM<sub>2.5</sub>/PM<sub>10</sub> ratios ranged from 0.49 to 0.94 indicating that high percentage was within the PM<sub>2.5</sub> size fraction during the sampling period. Fine particulate of the PM<sub>2.5</sub> size fraction generally emanates from thermal combustion process of gasoline and diesel fueled automotive engines. Since Farmgate site is located at one of the most congested traffic intersection and heavily

influenced by emissions from buses, trucks, baby taxis and cars, these results are not unexpected. Also, sampling occurred during the wet season when road dust influences are minimized. Therefore, most of the particulate emissions at Farmgate are produced by the vehicular tailpipe emissions.

## **Chemical Speciation of Filter Mass**

Filter mass from the samples were analyzed at the Desert Research Institute, Reno, Nevada, USA according to the standard laboratory protocol established by the US EPA. Elemental concentrations of Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Pb, etc. were determined from Teflon filter mass by using Particle Induced X-ray Emission (PIXE) and X-ray Fluorescence (XRF) techniques. By combining the measured variables for Teflon filter, the concentrations of all major fine mass except nitrate can generally be determined. The quartz filter was analyzed for carbon measurement using the Thermal Optical Reflectance (TOR) combustion method. The samples were heated in steps and evolved CO<sub>2</sub> measured. The sulfate on the impregnated quartz filter following the Teflon filter was analyzed by ion chromatography to give the concentration of SO<sub>2</sub>. The average precision of selected measured variables, based on the ratio of average precision to average concentrations are somewhat satisfactory, although could be minimized with proper implementation of QA/QC procedures during ambient sampling, storage, and transportation.

Table 2 summarizes chemical concentration of each species identified in the ambient filters. The most abundant PM chemical components in Dhaka were organic carbon, sulfate, elemental carbon, nitrate, geological elements (Al, Ca, Fe, Ti, and Si) and sodium. These are the same most abundant species found in most urban areas.

Organic carbon consists of hundreds, possibly thousands, of separate compounds. Vehicle exhaust, residential and agricultural burning, cooking, fuel combustion, road dust, and particle formation from heavy hydrocarbon (C<sub>8</sub> to C<sub>20</sub>) gases are the major sources of organic carbon. Elemental carbon is black, often called “soot.” Elemental carbon contains pure, graphite carbon, but it also contains high molecular weight, dark-colored, non-volatile organic materials, such as tars, biogenics, and coke. Elemental carbon usually accompanies organic carbon in combustion emissions with diesel exhaust being the largest contributor.

Suspended dust consists mainly of oxides of aluminum, silicon, calcium, titanium, iron, and other metal oxides. The precise combination of these minerals depends on geology of the area and industrial processes, such as steel making, smelting, mining, and cement production. Geological material is mostly in the coarse particle fraction, and typically constitutes ~50% of PM<sub>10</sub> while only contributing 5 to 15% of PM<sub>2.5</sub>.

Trace metal concentrations often indicate the presence of specific source contributions. Lead and bromine originate from vehicle exhaust systems that are used with leaded gasoline. Similarly, vanadium and nickel, often present in emissions from residual oil

combustion. Potassium is often associated with vegetative burning, similar to that from prescribed burns, forest fires, residential wood combustion, and cooking.

Ammonium sulfate, ammonium bisulfate and sulfuric acid are the most common forms of sulfate found in atmospheric particles, resulting from conversion of gases to particles. These compounds are water-soluble and reside almost exclusively in the PM<sub>2.5</sub> size fraction. Ammonium nitrate is often found to be the most abundant nitrate compound.

## **Secondary Particulate Emissions**

Based on the criteria suggested by Chow et al. (1993), that a ratio of organic carbon (OC) to elemental carbon (EC) in excess of 2 indicates the presence of secondary aerosols. It is resolved from examination of the speciated data that aerosols in the Dhaka ambient incorporate a significant aerosol component. Secondary aerosols are not directly emitted by sources as particulate matter; rather they are formed in the atmosphere via complex chemical reactions of precursor gases.

Gaseous emissions of precursor gases such as sulfur dioxides, nitrogen oxides, and ammonia converts to particulate of ammonium nitrate, ammonium sulfate, ammonium bisulfate, and sulfuric acid. Sulfur dioxide gas converts to particulate sulfate through gaseous and aqueous phase transformation pathways. In the gas phase pathways, sunlight induces photochemical reactions that create hydroxyl radicals that react with a wide variety of atmospheric constituents. Transformation rate ranges from 0.1% per hour to about 5% per hour. The transformation rate appears to be controlled more by the presence of hydroxyl radical and its competing reactions with other gases than by the sulfur dioxide concentration. In the presence of fogs or clouds, sulfur dioxide dissolves in droplets where it experiences reactions that are much faster than the gas-phase reaction. When ammonia is also dissolved in the droplet, the sulfuric acid is neutralized to ammonium sulfate. As relative humidity decreases below 100% (i.e., the fog or cloud evaporates), the sulfate particle is present as a small droplet that includes a portion of liquid water. As relative humidity further decreases, the droplet evaporates and a small, solid particle remains. Aqueous transformation rates of dissolved sulfur dioxide to sulfate are 10 to 100 times faster than gas-phase rates.

In the presence of ammonia, nitric acid is neutralized to particulate ammonium nitrate. Conversion rates for nitrogen dioxide to nitric acid range from less than 1% per hour to 90% per hour; typically five to ten times the conversion rates for sulfate formation. These conversion rates are significant during both daytime and nighttime hours, in contrast to the gas-phase sulfate chemistry that is most active during the day.

Sulfur dioxide to particulate sulfate and nitrogen oxides to particulate nitrate reactions competes with each other for available hydroxyl radicals and ammonia. Ammonia reacts preferentially with sulfuric acid to form ammonium bisulfate and ammonium sulfate, and amount of ammonium nitrate formed is only significant when the total ammonia exceeds the sulfate by a factor of two or more on a mole basis. Reducing sulfur dioxide

emissions might result in ammonium nitrate increases that exceeds the reductions in ammonium sulfate where there is dearth of ammonia.

There is a computer model currently being used in the US called “Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE)”, which can apportion sodium, nitrate, sulfate, ammonium, and chloride among gas, liquid, and solid phases using thermodynamic equilibrium theory. It is recommended that further analysis of the chemical speciation data presented in this paper must include an application of SCAPE modeling to understand the relative fraction of each particulate emissions category.

## Conclusion

- The Farmgate site has shown the maximum ambient level, as high as 526 microgram of PM<sub>2.5</sub> per cubic meter of air volume. This level is more than eight folds higher than the US EPA standard of 65 microgram per cubic meter. The fine PM<sub>2.5</sub> size pollutants are primarily emitted by combustion processes and automobile emissions. As Farmgate is considered one of the most congested traffic intersections in Dhaka, such an extremely high PM<sub>2.5</sub> level is the direct result of vehicular emissions.
- Source attribution of ambient aerosols in Dhaka indicates that contribution from vehicle emissions, secondary aerosols, and soil/road dust dominated fine aerosol mass during the sampling period.
- High loading of Al, Ca, Fe, K, Si, and organic carbon is interpreted as being indicative of soil/road dust contribution.
- Significant loading of K, Na, NH<sub>4</sub>, Ni, NO<sub>3</sub>, and S showed presence of high amount of secondary aerosols.
- Significant loading of Pb, Br, S, and Zn represents direct vehicular emissions.

In order to apportion specific source category contribution, future analysis of the speciated data must include receptor modeling, Chemical Mass Balance (CMB) modeling, trajectory analysis, spatial and temporal analysis, regression analysis, and SCAPE simulations. Results from these studies will enable authorities to devise appropriate emission reduction measures.

**Acknowledgement:** The author gratefully acknowledges the service of DRI laboratory, particularly gracious assistance of Dr. Judith Chow, in analyzing all of the filters at no cost. Author also thanks Mr. John Core for making the filters available and DOE personnel for their effort in collecting the samples.

**Table 2: Minimum, Maximum, and Average of Chemical Concentrations of Species Identified in Dhaka Ambient filters (microgram/cubic meter)**

Species	Minimum	Maximum	Average
CL-	0.9591	2.4731	1.4248
NH3+	0,4806	4.6651	1.4211
SO4-2	1.9292	13.4715	5.2670
NH4+	0.0384	1.3279	0.3268
K+	0.3552	3.0455	0.5885
OC (organic carbon)	12.9309	315.383	54.9708
EC (elemental carbon)	3.727	57.4187	16.3521
TC (Total Carbon)	18.9359	372.8017	71.3181
Na	0	1.0934	0.5421
Mg	0	0.8378	0.1460
Al	0	2.0824	0.2490
Si	0.702	7.0248	0.9447
P	0	0.1025	0.0336
S	0.056	3.8164	0.8186
Cl	0	0.4756	0.1229
K	0	1.5127	0.3442
Ca	0	2.8629	0.4002
Ti	0	0.2654	0.03719
V	0	0.0346	0.00549
Cr	0	0.0181	0.00586
Mn	0	0.064	0.01272
Fe	0.0314	3.4433	0.45141
Co	0	0.0202	0.00265
Ni	0	0.018	0.00241
Cu	0	0.0677	0.011445
Zn	0.0012	0.9295	0.148845
Ga	0	0.0233	0.003489
As	0	0.0445	0.00564
Se	0	0.0065	0.000449
Br	0	0.5996	0.052711
Rb	0	0.0115	0.010128
Sr	0	0.115	0.001511
Y	0	0.0146	0.003749
Zr	0	0.0629	0.003272
Mo	0	0.0129	0.002026
Pd	0	0.0905	0.001806
Ag	0	0.1258	0.016287
Cd	0	0.1469	0.02666
In	0	0.0961	0.042887
Sn	0	0.0195	0.021696
Sb	0	0.1212	0.001428
Ba	0	0.2719	0.011381
La	0	0.7497	0.036681
Au	0	0.0382	0.147485
Hg	0	0.0226	0.009587
Tl	0	0.0105	0.001345
Pb	0.0012	1.209	0.001445
U	0	0.0126	0.197434
NH4SO4	0.65014	3.4641	0.0013
(NH4)2SO4	1.01283	5.5314	1.42341
			2.413619