Chemical Characterization of PM$_{10}$ in Agra, a Semi-arid Region

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Abstract

Monitoring of ambient PM$_{10}$ has been carried out at St. John’s College, Agra (a traffic site) during May to September 2006. The average mass concentration of PM$_{10}$ was found to be 131µg m$^{-3}$. The average total water soluble particulate load (total anions and cations) is 21.4 µg m$^{-3}$. Particulate NO$_3$ and SO$_4$ have the highest concentration (approximately 47% of total soluble), suggesting that anthropogenic activities play important roles in controlling these particulate concentrations. The calculated ‘Σcation/Σanion’ ratio (1.4) indicates that particulate matter is an alkaline in nature and suggests that SO$_4$, NO$_3$ and Cl are neutralized. However, without taking into account for Ca and Mg, the calculated ‘cation/anion’ ratio reduces to 0.7 indicating that Ca and Mg ions act as main neutralizers of particulate acidity.

Introduction

Recent epidemiological studies have shown a consistent association of the mass concentration of urban air thoracic particles (PM$_{10}$ - 50% cutoff diameter at 10 µm), and its subfraction fine particles (PM$_{2.5}$ - 50% cutoff diameter at 2.5 µm), with mortality and morbidity among cardiorespiratory patients (WHO, 2003). Besides the health effects, particulate matter also influences many atmospheric processes including cloud formation, visibility, solar radiation and precipitation, and participates a major role in acidification of clouds, rain and fog (Celis et al., 2004). Ambient particulate matter may be the carriers of acidic or toxic species (e.g., heavy metals, acids and carcinogenic organic compounds) and may have detrimental effects on human health and ecosystems (Cheng et al., 1996). Thus, atmospheric particulate matter can alter climate, biogeochemical cycles and chemistry of atmosphere.

Sources of the different particles in the atmosphere include wind blown dust, fuel combustion and secondary organic aerosol formation (Pinker et al., 2001). Recent studies suggest that automobile exhaust particles particularly diesel exhaust are becoming a more prominent component in urban sites (Harrison and Yin, 2000). Motor vehicles are the largest source of particulate matter (particulate matter ≤ 10 µm in aerodynamic diameter) (Lee et al., 1999). In an urban environment, steep increase in vehicular population has resulted in corresponding increase in pollutants emitted by these vehicles. In order to understand the sources, behaviour and mechanism of formation of particle (i.e. PM$_{10}$) in the atmosphere it is important to measure the chemical composition of particulate matter. In the present communication, we report the mass concentrations of PM$_{10}$ and its water soluble ionic species collected at semi-arid region.

Experimental

Measurement of PM$_{10}$ was conducted on the roof of St. John’s College (SJC) building about 8 m above the ground. The site is situated in the heart of the Agra city. It is a major residential and commercial area. The sampling site lies by the side of a road that carries mixed vehicular traffic. Traffic volume of the road is extremely high, which is more than 1,00,000 vehicles per day. PM$_{10}$ samples were collected by respirable dust sampler (APM 460DX) with the cut point of 10 µm. The PM$_{10}$ sampler was operated at a flow rate of 1.0 m$^3$ min$^{-1}$. The mass of PM$_{10}$ was determined by the difference in weights before and after sampling.
For the analysis of water soluble fraction, the filters were extracted by ultrasonic bath in 50 ml de-ionised water for 1h. These extracts were filtered through Whatman 41 filters into two pre washed polypropylene bottles. One part was refrigerated and used for the analysis of ions of F, Cl, NO₃, SO₄ and NH₄ and the other part was acidified with HNO₃ for the analysis of ions of Na, K, Ca and Mg. Major inorganic anions (F, Cl, NO₃ and SO₄) were analysed by ion chromatography. The cations were determined by atomic absorption spectrophotometer. NH₄ was determined colorimetrically using Indophenol blue method.

Results and Discussion

The average mass of total PM₁₀ along with concentrations of major water soluble inorganic ions (F, Cl, NO₃, SO₄, Ca, Mg, Na, K and NH₄) are presented in Table 1. Average mass concentration of PM₁₀ is found to be 131 µg m⁻³ at St. John’s College, Agra. Measured concentration of PM₁₀ is exceeded by 30% of the Indian National Air Quality standard (100 µg m⁻³) and approximately by 70% of the WHO standard (50 µg m⁻³) which suggests that there is a definite need to measure and control the particulate matter. The contribution of water soluble ionic components is also presented in Table 1. The average total water soluble particulate load (total anions and cations) is 21.4 µg m⁻³. Among the ionic components NO₃ contributed the maximum to water soluble PM₁₀ mass (23.6%) followed by SO₄ (23%) and Cl (15%). The cations Na, K, Ca and Mg accounted (32%) of the total water soluble mass. The lower contributions of Ca and Mg suggest that they occur mainly as insoluble ions of CO₃, HCO₃ and SiO₂.

The highest concentration is observed for NO₃ (5 µg m⁻³) in PM₁₀. The present site is nearby a busy road therefore sufficient amount of NOₓ is present due to vehicular emissions. Particulate NO₃ may thus be formed by the absorption and subsequent reaction of NO₂ on the soil particles. SO₄ is another major constituent of PM₁₀ comprising 23% in PM₁₀. At this site particulate sulphate may be formed through oxidation of SO₂ (emitted from the vehicular emissions) through the homogeneous and heterogeneous reactions on the surface of basic soil particles. The present site belongs to semi arid region thus local terrestrial sources may be affecting the composition of PM₁₀. To see the effects of local sources on PM₁₀, firstly soil fraction has been calculated. In Agra, a significant fraction of Ca and Fe is emitted from the anthropogenic activities (ferrous and non ferrous foundries) (CUPS, 1987), therefore we chose Mg as a reference element assuming all suspended Mg to be soil origin. The ratios of various ions with respect to Mg in PM₁₀ and soil are presented in Table 2. It is found that Cl/Mg, SO₄/Mg and NO₃/Mg are much higher than the soil ratios. Higher ratios suggest that besides the soil other sources also contribute. Using Mg as a tracer of soil, excess ions (i.e. non-soil ions) can be calculated as Ions_{nonsoil} = [Ions]_{PM10} - [Mg]_{PM10} x soil ratio (Parmar et al., 2001). According to this calculation, it is found that 15% of Cl, 40% of SO₄ and 75% of NO₃ is contributed from the non soil or anthropogenic activities. These results confirm that heterogeneous reactions of SO₂ and NO₂ on soil particles are the source of higher particulate SO₄ and NO₃ in PM₁₀.

The equivalent ratio of NH₄/SO₄+NO₃ is an indicator of neutralization. If all the particulate NO₃ and SO₄ are neutralized by the NH₄, then the equivalent ratio would be equal to unity. At this site, the ratio is much less than 1.0. The observed ratio (0.3) suggests that the sulphate and nitrate particulates are far higher than the neutralization equilibrium by ammonium. The Q value can be used as an indicator of the degree of neutralization of total particulate matter and calculated as:

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Q = \frac{[\text{Ca}] + [\text{Mg}] + [\text{Na}] + [\text{K}] + [\text{NH}_4]}{[\text{F}] + [\text{Cl}] + [\text{NO}_3] + [\text{SO}_4]} \quad \text{(all concentrations are in equivalent)}
\]

The average value of Q is 1.4 indicates that the particulate as a whole appear to be an alkaline mode. The largest contribution for the neutralization results are from the high concentrations of Ca followed by Mg. Without Ca and Mg ‘Cation/anion’ ratio of Q is significantly reduced. The observed Q is 0.7 which suggests that Ca and Mg plays important role in neutralizing the particulate acidity at this site.
Conclusions

The study reveals that the mass concentration of PM$_{10}$ is higher than the Indian standards suggesting more efforts should be taken for regulation. The water soluble fraction of PM$_{10}$ is mainly composed of NO$_3$, SO$_4$ and Cl associated with NH$_4$, Na, Ca, Mg and K. It was found that the ratios of NO$_3$/Mg, SO$_4$/Mg and Cl/Mg in PM$_{10}$ are higher to local soil ratios. On calculating the non-soil contribution of NO$_3$ and SO$_4$ it was found that 75% of the NO$_3$ and 40% of SO$_4$ are originated from the anthropogenic activities (i.e. vehicular emissions). The calculated ratio of $\Sigma$cation/ $\Sigma$anion (1.4) shows that the Ca and Mg plays important role in the neutralizing the particulates at this site.

Acknowledgement

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References

Table 1: Average concentrations of different water soluble components in PM$_{10}$

<table>
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<tr>
<th>Species</th>
<th>Concentration (µg m$^{-3}$)</th>
<th>% contribution</th>
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<tbody>
<tr>
<td>F</td>
<td>0.74 ± 0.2</td>
<td>3</td>
</tr>
<tr>
<td>Cl</td>
<td>3.2 ± 0.7</td>
<td>15</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>5.0 ± 1.1</td>
<td>24</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>4.9 ± 0.9</td>
<td>23</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>0.7 ± 0.2</td>
<td>3</td>
</tr>
<tr>
<td>Ca</td>
<td>2.1 ± 0.6</td>
<td>10</td>
</tr>
<tr>
<td>Mg</td>
<td>1.2 ± 0.5</td>
<td>6</td>
</tr>
<tr>
<td>Na</td>
<td>2.0 ± 0.7</td>
<td>9</td>
</tr>
<tr>
<td>K</td>
<td>1.5 ± 0.6</td>
<td>7</td>
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Table 2: Ionic ratios of water soluble components of PM$_{10}$ and soil

<table>
<thead>
<tr>
<th></th>
<th>Cl/Mg</th>
<th>SO$_4$/Mg</th>
<th>Ca/Mg</th>
<th>K/Mg</th>
<th>NO$_3$/Mg</th>
<th>Na/Mg</th>
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<tbody>
<tr>
<td>PM$_{10}$</td>
<td>2.7</td>
<td>4.1</td>
<td>1.8</td>
<td>1.2</td>
<td>4.2</td>
<td>1.7</td>
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<tr>
<td>Soil*</td>
<td>1.9</td>
<td>2.5</td>
<td>3.7</td>
<td>1.7</td>
<td>0.97</td>
<td>2.1</td>
</tr>
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</table>

* Values taken from Parmar et al., 2001