C-O-3

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

P. Gursumeeran Satsangi, A. Kulshrestha*, A. Taneja* and P.S.P. Rao

Indian Institute of Tropical Meteorology, Pashan, Pune- 411 008
*Department of Chemistry, St. John's College, Agra – 282 003.

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, biogechemical 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, NO_3, SO_4 and NH_4 and the other part was acidified with HNO_3 for the analysis of ions of Na, K, Ca and Mg. Major inorganic anions (F, Cl, NO_3 and SO_4) were analysed by ion chromatography. The cations were determined by atomic absorption spectrophotometer. NH_4 was determined colorimetrically using Indophenol blue method.

Results and Discussion

The average mass of total PM_{10} along with concentrations of major water soluble inorganic ions (F, Cl, NO_3, SO_4, Ca, Mg, Na, K and NH_4) are presented in Table 1. Average mass concentration of PM_{10} is found to be 131 µg m^{-3} at St. John's College, Agra. Measured concentration of PM_{10} 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 NO_3 contributed the maximum to water soluble PM_{10} mass (23.6%) followed by SO_4 (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 CO_3, HCO_3 and SiO_2.

The highest concentration is observed for NO_3 (5 µg m^{-3}) in PM_{10}. The present site is nearby a busy road therefore sufficient amount of NO_x is present due to vehicular emissions. Particulate NO_3 may thus be formed by the absorption and subsequent reaction of NO_2 on the soil particles. SO_4 is another major constituent of PM_{10} comprising 23% in PM_{10}. At this site particulate sulphate may be formed through oxidation of SO_2 (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 PM_{10}. To see the effects of local sources on PM_{10}, 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 PM_{10} and soil are presented in Table 2. It is found that Cl/Mg, SO_4/Mg and NO_3/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 SO_4 and 75% of NO_3 is contributed from the non soil or anthropogenic activities. These results confirm that heterogenous reactions of SO_2 and NO_2 on soil particles are the source of higher particulate SO_4 and NO_3 in PM_{10}.

The equivalent ratio of NH_4/SO_4+NO_3 is an indicator of neutralization. If all the particulate NO_3 and SO_4 are neutralized by the NH_4, then the equivalent ratio would be equal to unity. At this site, the ratio is much less than 1.0. The observed ration (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:

$$Q = \frac{[Ca] + [Mg] + [Na] + [K] + [NH_4]}{[F] + [Cl] + [NO_3] + [SO_4]} \quad \text{(all concentrations are in equivalent)}$$

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 Σcation/ Σanion (1.4) shows that the Ca and Mg plays important role in the neutralizing the particulates at this site.

Acknowledgement

References

1. Celis, J.E., Morales, J.R., Zaror, C.A., Inzunza, J.C., 2004. A study of the particulate matter PM_{10} composition in the atmosphere of Chillan, Chile. Chemosphere 54, 541– 550.
2. Cheng, M.D., Gao, N., Hopke, P.K., 1996. Source apportionment study of nitrogen species measured in southern California in 1987. Journal of Environmental Engineering 122, 183–190.
3. Control of Urban Pollution Series, 1987. Status of air quality in Agra region. CUPS 15: 19-20. Central Pollution Control Board, New Delhi, India.
4. Harrison, R.M., Yin, J.X., 2000. Particulate matter in the atmosphere: which particle properties are important for its effects on health? Science of the Total Environment 249, 85–101.
5. Lee, H.S., Kang, C.M., Kang, B.W., Kim, H.K., 1999. Seasonal variations of acidic air pollutants in Seoul, South Korea. Atmospheric Environment 33, 3143–3152.
6. Parmar R.S., Satsangi, G.S., Kumari, M., Lakhani A., Srivastava S.S. and Prakash S., 2001. Study of size distribution of atmospheric aerosol at Agra. Atmospheric Environment 35, 693-702.
7. Pinker, R.T., Pandithurai, G., Holben, B.N., Dubovik, O., Aro, T.O., 2001. A dust outbreak episode in Sub-Sahel West Africa. Journal of Geophysical Research-Atmospheres 106, 22923–22930.
8. World Health Organization (WHO): Health aspects of air pollution with particulate matter, ozone and nitrogen dioxide. Report on a WHO Working Group, Regional Office for Europe; Bonn, Germany 13–15 January 2003. EUR/03/ 5042688. Available also at http://www.euro.who.int/ document/e79097.pdf.

Table 1: Average concentrations of different water soluble components in PM_{10}

Species	Concentration ($\mu g\ m^{-3}$)	% contribution
F	0.74 ± 0.2	3
Cl	3.2 ± 0.7	15
NO_3	5.0 ± 1.1	24
SO_4	4.9 ± 0.9	23
NH_4	0.7 ± 0.2	3
Ca	2.1 ± 0.6	10
Mg	1.2 ± 0.5	6
Na	2..0 ± 0.7	9
K	1.5 ± 0.6	7

Table 2: Ionic ratios of water soluble components of PM_{10} and soil

	Cl/Mg	SO_4/Mg	Ca/Mg	K/Mg	NO_3/Mg	Na/Mg
PM_{10}	2.7	4.1	1.8	1.2	4.2	1.7
Soil*	1.9	2.5	3.7	1.7	0.97	2.1

* Values taken from Parmar et al., 2001