STUDY OF CHEMICAL COMPOSITION OF ATMOSPHERIC AEROSOL OF MONSOON RAINWATERS IN CAPITAL DEVELOPMENT AUTHORITY AREA OF ISLAMABAD, PAKISTAN

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ABSTRACT: This paper presents the useful information about the level and chemical composition of the aerosol pollutant particulates matter at Capital Development Authority in Islamabad, the capital of Pakistan. The rain water samples were collected during the period of summer July - August 2008 (Monsoon). Twenty-one samples were collected and analyzed by Ion – Chromatographic Technique for the determination of anions and cations, physical parameters, pH , conductivity and turbidity were studied while total carbon (TC) was determined by Carbon Analyzer . The results obtained were compared to the WHO standard. It was observed that the chemical composition of the rain waters (aerosols particulates) of Islamabad are substantially deteriorated and do not accede to the required standards of World Health Organizations. Further the data will serve as base line level for other workers in future.

Keywords: Chemical composition ; Precipitation ; pH; Trace elements ; Organic carbon

INTRODUCTION

Urbanization, industrialization and economic growth resulted in a profound deterioration of urban air quality [1,2]. Modernization and enhanced industrial activities led to the increased use of fossil fuels and their derivatives, particularly in developing countries like Bangladesh. Concern about atmospheric particulate pollution in urban region is getting growing importance worldwide [3]. Urban areas are mainly affected by suspended particles, which pose a serious risk to human health [4]. Several epidemiological studies have indicated a strong association between elevated concentrations of inhalable particles (PM10 and PM2.5) and increased mortality and morbidity [5-7]. It also influences many atmospheric processes including cloud formation, visibility, solar radiation and precipitation, and plays a major role in acidification of clouds, rain and fog [8-10]. Particulate matter pollution in the atmosphere primarily consists of micron and sub-micron particles from the anthropogenic - motor vehicles, biomass, fossil fuel burning, and natural sources - windblown soils and sea spray [11]. The characterization of the fine particles is becoming more important to governments, regulators, and researchers due to their potential impact on human health [12], their ability to travel thousands of kilometers across countries, and their influence on climate forcing and global warming [13].

The Indo-Asian aerosols impact the radiative forcing through a complex set of heating (positive forcing) and cooling (negative forcing) processes. Clouds and black carbon emerged as the major players [14]. The magnitude of the aerosol effect, directly as well as indirectly, is crucially dependent upon the amount of hygroscopic and of strong absorbing material in the particulate matter. Aerosol plumes extending south of the Indian sub-continent during the dry monsoon season were considered to origin primarily from biomass smoke, but a detailed analysis of elemental ratios (elemental carbon (EC)/organic carbon (OC), EC/K) revealed that the far majority of the EC as well as OC in the plume were from fossil fuel sources, e.g. coal, oil and diesel fuel combustion [15-16] . Also an earlier study of the organic aerosol in Kuala Lumpur, Malaysia [17] came to the conclusion that burning of biomass is not a major factor contributing to OC in samples of elevated aerosol loads, while indicators for fossil fuel contribution were present in elevated concentrations. Generally from the data for EC/total carbon (TC) and EC/K ratios, allowing in a first order approximation to derive biomass and fossil fuel involvement in the carbonaceous fraction of the aerosol [16] , are available only to a dozen of sites in Eastern Asia. For example in assumptions about the types of aerosol emission in Pakistan up to now have been made with considering similarities in the fuel use of India, Pakistan and Bangladesh [18] . In fact, for Southeast Asia until now respective aerosol compositional data are available only for Lahore, Pakistan; Mumbai, India and for sites in Japan and Korea.

Since for the Indian sub-continent respective aerosol information is available in very less number of cities like Lahore and Mumbai but here the data presented is of Islamabad in which focus has been made on the aerosol chemical composition with regard to carbonaceous aerosol species, soluble major ions, and selected anions and cations during pre-monsoon meteorological conditions.

The city, Islamabad is of great importance as it is the capital of Pakistan (surrounded by Margalla hills) and apart from the local population, there is also a significant number of foreign multinationals serving in embassies and in different institutions. Owing to the developing nature of this region, there is an on-going increase in other anthropogenic activities around the cities. Increasing number of industries, transportations, agriculture affects the air environment. This study is conducted to assess the level of trace elements in the atmosphere of Islamabad, Pakistan. Islamabad is congested with a large number of motor vehicles, including both public and private transportation. A high concentration of air pollutants such as black carbon in Islamabad city air has been reported by the earlier workers due to vehicular emissions, as well as biomass/coal burning for cooking and the brick kilns around the Islamabad city, are the main contributor to these emissions (Figure-1).

Figure-1 Biomass burning

The aim of this paper is to gain an initial understanding of the rainwater chemistry, to identify possible sources that contribute to its chemical composition and finally to establish a baseline data at an urban locality in peninsular Pakistan , where the proper data are not available.

MATERIALS AND METHOD

The aerosol sampling was carried out at the location Capital Development Authority of Islamabad, situated within the urban area with residential sectors in its surroundings. The suspended particulates samples were collected by low volume samplers as as given in Figure-2 and Table-1. The samplers were equipped with poly-carbonate open-face filter holders . Field blanks were determined for each sampling site and considered for the calculation procedures. The loaded filters were stored in clean Millipore Petri dishes and kept under refrigeration during the sampling period to minimize losses due to volatilization and evaporation. During the performing of the experiment the following materials were used; HNO_3, plastic containers , pH meter and conductivity meter, Turbidity meter, Ion – Chromatographic Instrument and Carbon Analyzer etc.

Ion analysis

Quartz fiber filter aliquots (3 punches of 10 mm ∅) were extracted for 20 min ultrasonically in 3.5 ml ultra-pure water. Anions (F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} and $C_2O_4^{2-}$) and cations (Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+}) were analyzed with ion chromatography. Details of the analytical method were given by [19] with the exception that an auto-sampler (Spark Holland Marathon) was used to deliver the samples instead of trace concentrator columns. Field blanks were determined for each sampling site and considered for the calculation procedures.

Total carbon (TC) was determined by Carbon Analyzer

Figure-2. Collection of samples

and similarly pH, conductance and turbidity were determined by pH meter, conductivity meter and turbidity meter respectively as given in Table-1

RESULTS AND DISCUSSION

The region of Islamabad is encompassed by forest and by major to minor industrial activities related to chemical and pharmaceutical based units, metal based units, brick and refractory kilns and lime oxidation and pulverization. Besides these, the mobile sources also contribute a significant amount of atmospheric pollutants.

Though a continental type of climate prevails in the region with four distinct seasons, winter from December , to February, Spring from March to May , and Summer from June to September where monsoon from July to August and Autumn from October to November, so, it is clear that the sampling site is mostly wet during the monsoon period (July to August) and dry in the summer The local ambient temperature (which is affected by solar radiation) starts to increase in May and reaches its maximum in June (approx. 43 °C) after which it decreases to a minimum of 13 °C during January, while the wind speed is varied between 18.9 km h^{-1} (during summer) and 2.5 km h^{-1} (during monsoon).

From the data of Table-1 , it is observed that alkalinity level is 5.7 due to lower temperature and high humidity on the regard of neutralization of acid while it was also found that the level turbidity is not that of the other heavy populated cities of Pakistan .

Sulfate, nitrate and calcium acted as the major contributors to the soluble ions in Islamabad . The measured concentrations of the soluble ions in Islamabad were within the range as shown in Table-2 and Figure-3. Balancing equivalents of cations and anions (data not shown) indicate the existence of excess alkaline material in the aerosols. Thus, the formation of nitrate is likely a result of photochemical formation of nitric acid in the Islamabad urban atmosphere and subsequent aerosol formation

Table-1. Physical parameters of aerosols particulates of rain waters of Islamabad

No.	Acc #	Sample Collected	# of Events	TOC (mg/l)	Cond. (us/cm)	pH (lab)	Turbidity (NTU)
	2008						
1	001	7/05	1	0.7656	41.3	5.94	1.33
2	002	7/07	1	0.7678	33.9	5.92	0.69
3	003	7/ 08	1	0.7255	19.5	5.95	0.74
4	004	7/09	1	0.337	46.4	5.97	1.07
5	005	7/12	1	0.6878	17.1	5.89	0.9
6	006	07/14	1	0.6287	103.6	5.72	1.38
7	007	07/15	1	0.724	23.3	5.65	0.85
8	008	7/16	1	0.3065	67	5.43	1.12
9	009	7/17	1	0.5181	53.8	5.91	0.55
10	010	07/17	1	0.7274	166.5	5.95	1.55
11	011	7/19	1	0.3353	44.9	5.9	1.02
12	012	07/20	1	0.5904	88.8	5.81	0.94
13	013	7/25	1	0.6812	137.8	5.79	0.19
14	014	7/28	1	0.7378	163.7	5.89	0.24
15	015	7/31	1	0.5444	144.4	5.91	1.19
16	016	8/1	1	0.306	46.7	5.79	0.61
17	017	8/4	1	0.4668	14.9	5.93	0.32
18	018	8/5	1	0.6316	17	5.75	0.91
19	019	8/5	1	0.7402	27.2	5.87	0.45
20	020	8/9	1	0.2684	32	5.95	0.85
21	021	8/12	1	0.6796	34.6	5.77	1.09

with excess aerosol alkalinity. The major sources of nitrate in Islamabad are NO_x emissions from traffic vehicles (54.5%) and brickfields and small industries (17.5%), [20] . Nitrate is only strongly correlated with chloride. The average ammonium concentration at the Islamabad was 1.86 µg m^{-3} . Particulate ammonium is formed by the neutralization of acidic species upon reaction with ammonia. The volatility of ammonium compounds (e.g. chloride, nitrate) at higher temperature can cause losses of particulate ammonium.

Sources for particulate potassium are biomass combustion but also coal fly ash emissions and fugitive soil dust. Calcium is a constituent in coal fly ash but also in biomass smoke and, dependent on regional geology, a constituent of mineral dust. Calcium was the most abundant cation at Islamabad rather higher than at European cities but lower than in cities with heavy pollution, e.g. Jakratta, Bombay and Karachi . Average magnesium concentration at Islamabad which is comparable to concentrations at other Asian cities like Lahore and Mumbai . Magnesium showed strong correlation with sodium and chloride . The average concentration of sodium (1.27 µg m^{-3}) was also within the range but Sodium was strongly correlated with magnesium and chloride. The average chloride concentration at the Islamabad lies at the lower end of other South Asian cities. Islamabad is the capital of Pakistan, therefore, a considerable local contribution at Islamabad can be assumed. Relatively elevated fluoride concentration levels were observed at the Islamabad. Emission sources might be brick production, glass furnaces, enameling, fertilizer production, and coal combustion.

In the current study carbonaceous materials, soluble ions, and trace elements were analyzed. From the major components only insoluble mineral components, e.g. from soil dust, mineral components of fly ash, street abrasion and resuspension, dust from construction activities, etc., based on silicious and aluminous compounds, and aerosol humidity were excluded. The sum of analyzed components thus reflects the aerosol composition without the insoluble mineral components. The insoluble mineral components are generally enriched in the size fraction >2 µm aerodynamic diameter and are typical components of the coarse aerosol fraction [21] . Aerosol humidity is usually not determined analytically and comprised around 20% of the ammonium sulfate concentration in aerosol in South Africa [22] .

Careful observation of correlation coefficients among the ionic components suggests that NaCl, $CaSO_4$, $MgSO_4$, $MgCl_2$, HNO_3, NH_4NO_3, NH_4SO_4 and $(NH_4)_2SO_4$ are predominant species combinations. They may be formed in the atmospheric water droplets by scavenging of aerosols and reaction of gaseous species. The partial dissolution of

Table-2.Anions and Cations of aerosols particulates of rain waters of Islamabad through Technique of Ion- Chromatography

No.	Acc #	Sample Collected	# of Events	NH_4^+ (ug/l)	F^- (ug/l)	Cl^- (ug/l)	NO_2^- (ug/l)	NO_3^- (ug/l)	SO_4^{2-} (ug/l)	$C_2O_4^{2-}$ (ug/l)	Ca^{2+} (ug/l)	Mg^{2+} (ug/l)	Na^+ (ug/l)	K^+ (ug/l)
1	001	7/05/08	1	24. 5	0.01	0.49	0.01	0.08	0.01	0.01	7326	266	697	469
2	002	7/07/08	1	1755	0.01	0.27	0.01	0.02	0.01	0.01	5371	139	572	505
3	003	7/ 08/08	1	1400	0.01	0.14	0.01	0.01	0.01	0.01	2648	43	309	295
4	004	7/09/08	1	2320	0.01	0.75	0.01	0.01	0.87	0.01	6271	349	942	625
5	005	07/12/08	1	2244	0.01	0.14	0.01	0.01	0.01	0.01	1516	24. 5	249	249
6	006	07/14/08	1	24.5	0.01	0.15	0.01	0.11	0.01	0.01	16301	1973	2766	2170
7	007	07/15/08	1	1943	0.01	<.10	0.01	0.01	0.01	0.01	2968	137	324	189
8	008	07/16/08	1	24.5	0.01	0.19	0.01	0.04	0.23	0.01	10494	412	1139	1856
9	009	07/17/08	1	1977	0.01	1.66	0.01	0.01	0.01	0.01	8329	320	979	365
10	010	07/17/08	1	782	0.01	0.72	0.01	0.08	0.23	0.01	29506	1402	4148	1782
11	011	07/19/08	1	1779	0.01	0.34	0.01	0.01	0.26	0.01	6747	230	906	580
12	012	07/20/08	1	1477	0.01	<.10	0.01	0.05	0.01	0.01	4012	225	737	666
13	013	07/25/08	1	24.5	0.01	0.62	0.01	0.06	0.01	0.01	21770	2086	4544	3104
14	014	07/28/08	1	4001	0.01	1.31	0.01	0.09	0.29	0.01	20100	3373	5594	2367
15	015	07/31/08	1	3200	0.01	0.65	0.01	0.1	0.3	0.01	20248	2814	3658	1491
16	016	08/01/08	1	3358	0.01	0.32	0.01	0.05	0.01	0.01	6606	140	227	348
17	017	08/04/08	1	1960	0.01	0.13	0.01	0.08	0.01	0.01	1393	24. 5	208	180
18	018	08/05/08	1	2079	0.01	0.35	0.01	0.01	0.01	0.01	758	24. 5	461	722
19	019	08/05/08	1	1932	0.01	0.18	0.01	0.01	0.01	0.01	1039	24. 5	1540	982
20	020	08/09/08	1	1939	0.01	0.28	0.01	0.01	0.2	0.01	0.01	39	287	348
21	021	08/12/08	1	1311	0.01	0.23	0.01	0.09	0.01	0.01	0.01	246	480	460

carbonate minerals such as calcite and dolamite is the most important reaction affecting the rainwater composition.

A majority of power generated in Pakistan (approximately 55%) is fueled by coal. There are several coalmines southwest of Islamabad that serve as a major supply for brick kiln industries that burn coal for manufacturing bricks in this region.

CONCLUSION

At the conclusion the aerosol studies of chemical composition of rainwater were carried out for the urban area of Islamabad, the capital of Pakistan for the period of July-August (Mosoon in Pakistan), which represents the very first contribution in the region to the knowledge of rainwater chemistry. Results suggest that the rainwater is typically alkaline, showing a very good correlation with Ca, which reveals that its acidity is being neutralized by soil components Ca, Mg and NH_4 and the ions are of non-sea salt origin. Among the ions, Ca makes the highest contribution followed by SO_4 and Mg indicating the incorporation of soil material into the rain, which reflects a major continental influence. The correlation studies and the comparison of major ion composition with other selected sites worldwide revealed that the rainwater ion composition is greatly influenced by terrestrial sources rather than anthropogenic and marine sources. The data serve further as aerosol profiles from an Asian mega-city, being of importance for source studies as well as for regional and global climate models.

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