High Volume Sampling and Dithizone Scrubbing-based Estimation of Aerosol Lead Levels at Islamabad, Pakistan

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Summary: Airborne lead levels in the local atmosphere of Islamabad, Pakistan, monitored at eight sampling sites, with low to moderately high traffic density, were determined by the flame AAS method using the high volume sampling and scrubbing techniques separately. Concentrated nitric acid based digestion method was employed for the dissolution of particulate matter collected on glass fiber filters, while the dithizone-carbon tetrachloride scrubbing method was used to trap the particulate matter at an air flow rate of 1.0 LPM. The lead levels determined by the scrubbing method ranged from 13 $\mu g/m^3$ to 90 $\mu g/m^3$ and from 30 $\mu g/m^3$ to 69 $\mu g/m^3$ as determined by the high volume sampling method. Climatic parameters, such as temperature, sunshine, wind speed, wind direction, pan evaporation and relative humidity, were included in the study, in relation to specific geographic terrain of the area, to evolve a probable correlation with the distribution of lead in the local atmosphere. Data on airborne lead distribution from other parts of the world are described and discussed.

Introduction

During recent years industrial development, urbanization efforts and human activities have been considered as significant factors towards understanding how aerosols affect climate. Aerosols are known to be formed from particles emitted from road vehicles, mining and quarrying, industrial combustion and power generation, all contributing to air pollution [1,2]. Numerous serious environmental issues have emerged from air pollution, especially due to the presence of toxic metals in the atmosphere, of which lead is well known to play a critical role. It is difficult to determine the natural level of lead in the air because of large variations in worldwide pollution from motor vehicle exhausts [3,4] and the weathering process, which alone causes mobilization of 180,000 tones of lead, mined each year the world over [5,6]. In addition, lead smelters cause air and water pollution, which may contaminate surface water reservoirs with airborne lead [7].

In Pakistan, like any other developing country, the industrial development and urbanization have not gone in pace with environmental safety, with the consequence that Islamabad, the capital city, is now confronted with the problems of housing and transportation due to fast emergence of industrial estates of varied types. Over the years, an industrial sector, and an industrial estate has been established in and around Islamabad to meet requirements of industrial commodities for a large population. The local urban population is now facing the typical adverse health effects of air pollutants which normally result from industrial emissions and increased vehicular traffic [8,9]. Earlier studies [10,11] have evidenced that the local atmosphere is now overburdened with aerosols rich in particulate matter, comprising heavy toxic metals, in addition to high levels of noxious gases [12,13].

An attempt has been made in the present study to develop a correlation between prevailing climatic parameters and the distribution of lead arising from vehicular activity in the local atmosphere of Islamabad, using the high-volume and air-scrubbing techniques. Eight air sampling and monitoring sites (Figure 1) with a widely varying traffic density were selected for this purpose. The pattern of traffic and the frequency of automobile operations in the city were kept in view while selecting the sites. Accordingly, typical urban routes, along with highways of Islamabad, were monitored for airborne lead distribution. The sampling times were fixed between 08:00 hrs to 16:00 hrs, thus including the morning and afternoon peak traffic hours. Airborne lead estimations were done by the Atomic Absorption Spectrophotometric method using the 217 nm resonance line. A Shimadzu AAS system, Model AA-670, with automate background compensation mode was used throughout this work. A high volume sampler was used to collect the aerosols on glass

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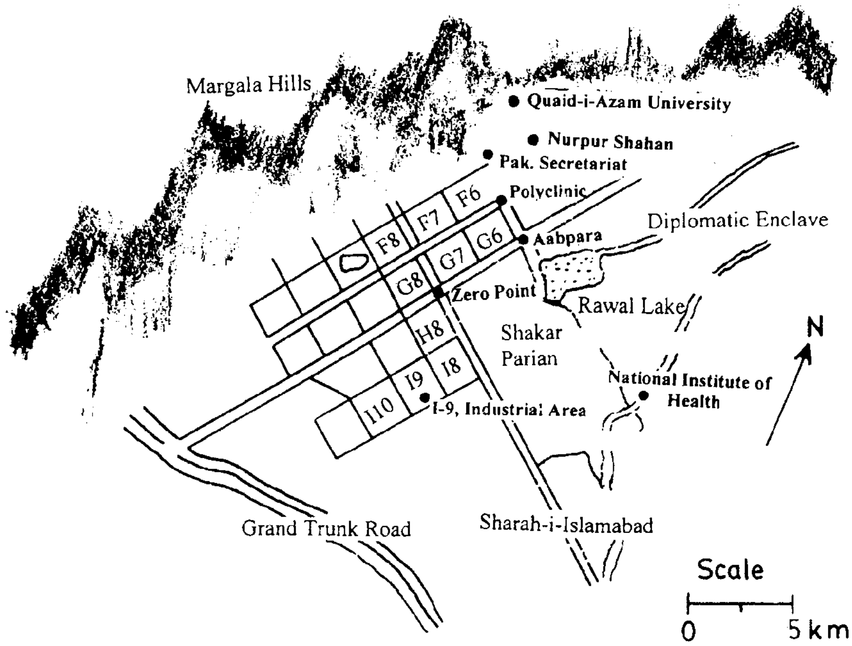

Fig. 1: Location map of sampling sites (•)

fiber filters digested subsequently in nitric acid. For the scrubbing method, dithizone-carbon tetrachloride medium was used to trap lead. The standard calibration method was used for quantification of the metal under optimized analytical conditions.

Results and Discussion

The airborne lead data pertaining to various sampling sites (Figure 1), determined by the two methods, are given in Table 1. Table 2 summarizes the relevant meteorological conditions during the sampling time. The data in Table 1 revealed that the pattern of distribution of lead concentration in local aerosols was quite divergent from site to site indicating large variations in atmospheric lead content. The lead levels determined by the scrubbing method (a, Table 1) ranged from 13 $\mu g/m^3$ to 90 $\mu g/m^3$, for site SS-8 and SS-2 respectively. The increasing order of the lead concentration at various sites was: SS-8 < SS-7 < SS-4 < SS-6 < SS-1 < SS-3 < SS-5 < SS-2.

The high volume sampling method (b, Table 1) yielded a pattern of lead distribution, almost 90% comparable with that obtained by the scrubbing method. Here again the highest concentration of lead (69 $\mu g/m^3$) was found for the site SS-2, followed by the same sequence of lead distribution as that for the former method. On the whole, the lead levels determined by the two methods were comparable with a very strong positive correlation, at $r^2 > 0.90$. The differences in the individual concentration of lead determined by the two methods could be considered on the basis of the time scale during which the two types of measurements were made. While for the scrubbing method, the sampling embraced an instantaneous 20 minute sampling, for the high volume method a prolonged sampling time (6-8 hr) was involved.

The meteorological parameters selected for the present study (Table 2) are well known to have a bearing on the mass transport and dispersion of particulate matters in the atmosphere. The temperature, sunshine, wind speed, wind direction, pan evaporation and relative humidity parameters listed in the Table indicate a typical dry season during the sampling period. Figure (2) depicts the observed relationship between airborne lead concentration and temperature pertaining to the sampling at given sites. The temperature dependence of lead was found to be a random phenomenon. A similar behaviour for sunshine may be seen in Figure

Table 1. Description of sampling sites and estimated lead levels by (a) scrubbing and (b) high volume methods

S. No.	Sample Code	Location	Vehicle Count (N/hr)	Lead Concentration ($\mu g/m^3$) (a)	(b)	Lead Concentration ($\mu g/m^3$) per 100 Vehicles (a)	(b)
1.	SS-1	Nurpur Shahan	780	52	40	6.67	5.13
2.	SS-2	Quaid-i-Azam University	360	90	69	25.00	19.17
3.	SS-3	National Institute Health	750	70	67	9.30	8.93
4.	SS-4	Aabpara	1800	38	39	2.11	2.17
5.	SS-5	Polyclinic	1500	75	62	5.00	4.13
6.	SS-6	I-9, Industrial Area	1680	46	41	2.74	2.44
7.	SS-7	Zero Point	930	36	30	3.87	3.23
8.	SS-8	Pak. Secretariat	370	13	45	3.51	12.16

Table 2. Relevant meteorological conditions prevailing during sampling

Sample Code	Temp. (°C)	Relative Humidity (%)	Sunshine (hours)	Wind Speed (km/hr)	Wind Direction	Pan Evap. (mm/day)
SS-1	29.5	28	2.1	3.2	E-W	4.6
SS-2	27.8	35	11.1	4.6	S-N	8.0
SS-3	30.9	35	9.3	5.8	E-W	10.2
SS-4	34.8	32	9.3	5.6	S-N	12.4
SS-5	32.5	47	8.2	7.4	S-N	11.6
SS-6	30.2	35	10.7	4.0	E-W	8.7
SS-7	31.2	43	10.7	3.6	S-N	10.1
SS-8	29.0	32	10.2	5.9	S-N	14.8

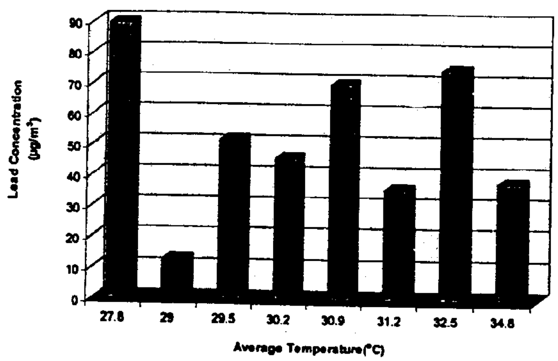

Fig. 2: Relationship between average lead concentrations and average temperature.

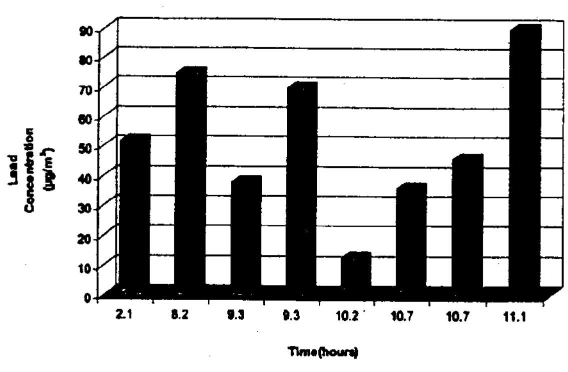

Fig. 3: Relationship between averae lead concentrations and sunshine.

(3) again showing no clear relationship between the two variables. A maximum sunshine of 11.1 hrs showed highest concentration of lead (90 $\mu g/m^3$), while for other comparable sunshine periods (10.7 hr) lead levels of 46 $\mu g/m^3$ and 36 $\mu g/m^3$ were observed, thus providing no obvious inter-relationship between the two variables. In case of atmospheric pollutants that undergo `photochemical reactions in the lower troposphere[14], the sunshine parameter is certainly useful towards quantitative distributions. However, in the present case, no such critical dependence on sunshine is observed.

The importance of wind speed towards air mass mixing at a given place is not considered in isolation from an auxiliary parameter, wind direction, which is considered to be a cause of depletion or accumulation of particulate pollutants from a given source to other sites under observation. Figure (4) brings out a divergent behaviour of wind speed: a wind speed of 5.8 km/hr carried a lead concentration of 70 $\mu g/m^3$; a comparable wind speed of 5.9 km/hr, on the other hand, carried only 13 $\mu g/m^3$ lead (Tables 1and 2). It is thus obvious that wind speed plays only a random role towards either enhancement or depletion of lead levels, even in instances where they govern the movement of gaseous and particulate pollutants in areas of high traffic density.

Likewise, the contribution of relative humidity towards the dispersion of lead was unclear and no

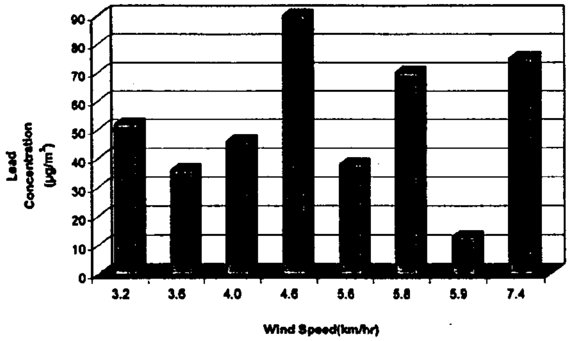

Fig. 4: Relationship between averae lead concentration and wind speed.

viable conclusion could be drawn between the two variables. For a given site and time, lead concentration increases with relative humidity and then declines, as shown in Figure (5). Within limits, low humidity is found to favour lead dispersion. On the whole, however, the specific role of higher humidity could not be ascertained since there was virtually no rainfall in Islamabad during the monitoring period.

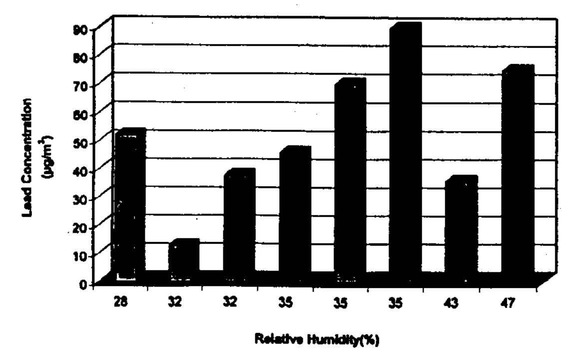

Fig. 5: Graphic representation of average lead concentrations vs relative humidity.

For example, lead levels in Taiwan were reported to range from 28 µg/m^3 to 783 µg/m^3 in a typical work place [15,16]. Also, some data from Ho Chi Minh City reflected a range of 90 µg/m^3 to 179 µg/m^3 lead in suspended particulate matter [17]. In respirable fraction, a level of 50 µg/m^3 lead has been reported with 150 µg/m^3 for the total lead dust [18]. However, for clean atmospheres, without any probable lead dust pollution as low concentrations of lead as 0.244 µg/m^3 have also been reported [19,20].

Experimental

A Lamotte Air Sampler (Dwyer instruments, Inc., Ind., U.S.A.) was used for collecting airborne lead in a scrubbing solution of dithizone in carbon tetrachloride at a flow rate of 1.0 LPM. The concentration of the scrubbing solution was 25 µmoles/L, and 25mL of this solution was used in each run. The scrubbing stock solution was prepared as follows.

A 0.025g portion of dithizone was dissolved in about 40mL of pure carbon tetrachloride. The deep-green solution was filtered into a separating funnel and extracted with 25mL of 0.075M ammonia solution twice. The organic phase was discarded, and the combined aqueous extracts were shaken with two 1mL portions of carbon tetrachloride. Then 50mL of carbon tetrachloride was added, and the solution was acidified with 2.5mL of 0.5M sulfuric acid with shaking. The organic phase was separated and washed with distilled water. This transfer of dithizone from carbon tetrachloride to ammonia solution and back was repeated four times, till the extraction with ammonia solution left a practically colorless organic phase. The dithizone solution was poured in a brown bottle along with 2.5mL of distilled water and 0.25mL of 0.5M sulfuric acid. The working solution was prepared by diluting 7mL of the stock solution up to 500mL with carbon tetrachloride. The concentration of the working scrubbing solution was found to be suitable to react completely with atmospheric lead levels. A scrubbing time of 20 minutes equivalent to 20 litres of sampled air furnished reproducible replicate samples.

A High Volume Air Sampler (GMWL Handi-Vol 2000) was used to collect airborne particulate matter on 8"×10" glass fiber filter (capable of retaining particles as small as 0.01 µm). The air flow rate was measured by a variable orifice meter, calibrated periodically to maintain on-site accuracy. The aerosols trapped on the filter were digested in 20mL 65% HNO_3, followed by treatment with 20mL 36% $HClO_4$ to oxidize any organic residue. The digested samples so obtained were aspirated onto the AAS system.

A lead stock solution (1000ppm) procured from E.Merck with certified high purity (>99.9%) was used for the preparation of working standards. Thoroughly washed and cleaned glassware was used to avoid any contamination problem. Inter-laboratory comparison of data was conducted at the Nutrition Division, National Institute of Health, Islamabad.

Conclusions

The present study indicated elevated levels of lead, ranging from 13 $\mu g/m^3$ to 90 $\mu g/m^3$, in the local atmosphere. Compared with typical urban atmospheric lead levels prevailing in other parts of the world, these lead levels are comparable with those with typical similar atmospheric environment as mentioned earlier. It is, therefore, obvious that the results of the present study reveal several orders of magnitude higher lead levels against these met with in countries where strict legislation towards the use of unleaded fuel is implemented.

The present study evidences that the local atmosphere of Islamabad is over-loaded with enhanced levels of lead probably for two obvious reasons. Firstly, the industrial area located in sector I-9 (Figure 1), caters a large vehicular transportation activity round the clock. The vehicular exhaust emissions, of which the lead particulate matter is a major component, escape freely and openly to the neighbouring sites. According to the meteorological office, for most time the winds blowing in the area are northerly, thus carrying the air masses towards the Margala Hills (Figure 1). Secondly, the Margala Hills probably act as a trapping zone for the high concentration pollutants, especially at night when the temperature falls and advective mixing of the air masses takes place due to temperature gradient in the Margala Hill Valley. The prevailing lead concentrations are only meagerly influenced by weather conditions, but to a greater extent by the enrichment of the metal levels by the trapping phenomenon due to which dispersion of the pollutants takes places in an undefined way in the area in close vicinity to the Hills.

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