Comparative High Volume and Scrubbing-Based Estimation of Aerosol Lead

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Summary: Aerosol lead levels were determined in the atmosphere of Rawalpindi, Pakistan, at eight sampling sites with low to high traffic density, using the standard high volume sampling and the modified dithizone scrubbing based techniques. Flame AAS method was employed to analyze aerosol particulates for Pb collected on glass fiber filters from a high volume sampler running on an 8-hourly basis. Nitric acid based digestion method was employed for the dissolution of particulate matter. In parallel, the dithizone-carbon tetrachloride scrubbing method was used to trap the particulate matter in solution at an inlet air flow rate of 1.5 LPM, at three pre-selected monitoring times: 8:00, 12:00 and 16:00 hrs. The Pb levels determined by the former technique ranged from 22 $\mu g/m^3$ to 57 $\mu g/m^3$ and by the latter from 18 $\mu g/m^3$ to 39 $\mu g/m^3$ on the same days. Meteorological parameters, such as temperature, wind speed, wind direction and relative humidity, were also recorded to evolve a probable correlation with the distribution and dispersion of Pb in the local atmosphere. The usefulness of the two techniques is herein highlighted for monitoring the metal levels in typical urban atmosphere. Data on airborne Pb distribution from other parts of the world are described and discussed.

Introduction

During the last three decades, climatic conditions prevailing in different parts of the world stand drastically changed due to industrial development, urbanization efforts and human activities. Aerosol and particulate matter emitted from vehicular exhaust, mining and quarrying, industrial combustion and power generation have affected human environment adversely. Aerosol behavior of vehicular exhaust plays a major role in air pollution [1,2]. Numerous studies on air pollution [3-5] have been carried out in relation to toxic trace metals dispersed by vehicular activity in the atmosphere. Of all the metals investigated, Pb is considered to play a critical role toward air pollution, in addition to soil and water pollution. It is difficult to estimate the level of Pb in the air because of large variations in worldwide pollution level from vehicular exhaust [6,7]. Weathering process causes mobilization of 180,000 tones of Pb per year and 2 million tones of Pb are mined each year throughout the world [8]. Lead smelters, lead storage battery and industry are also causatives of atmospheric Pb pollution [9]. It is known that automotive engines alone release 25-75 % of Pb into the atmosphere, depending on operating conditions. Therefore, the emission from motorcar exhausts is by far the most serious source of Pb pollution facing us today.

As a consequence, urban pollution everywhere is facing the typical adverse health effects of air pollutants, which normally result from increased vehicular traffic and industrial emissions [10, 11]. In Pakistan, like most other developing countries, the industrial development and urbanization have always gone unplanned. High levels of Pb have been reported in some preliminary studies carried out in the local area, with concentrations of Pb ranging between 24-130 $\mu g/ m^3$. Similarly, it has also been reported that the atmosphere of the twin cities of Islamabad/ Rawalpindi is rich in aerosol particulate matter [12, 13]. An attempt has been made in the present investigation to evaluate the present status of Pb distribution in the local atmosphere of Rawalpindi using the standard high volume air sampling techniques and to introduce a dithizone scrubbing based technique of routine use of independent Pb estimation in aerosols. A comparative out-look of the data obtained by the two techniques are then discussed to find out a possible correlation, and identifying to meteorological parameters governing the climatic conditions in the atmosphere.

Results and Discussion

The airborne Pb levels pertaining to the selected sampling sites and determined by the scrubbing-based and high volume sampling methods are given in Table-1. The reported concentrations in the Table are listed as averaged over the three sampling sequences, at 8:00, 12:00 and 16:00 hrs.

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Table-1: Description of sampling sites and estimated Pb levels by (a)* scrubbing and (b) high volume methods

Sample Code	Location	Vehicle Count (N/hr)	Lead Concentration ($\mu g/m^3$) (a)	(b)
SS-1	Sixth Road Chowk	760	34	29
SS-2	Saddar, GPO	1700	29	38
SS-3	Marir Hasan Chowk	1900	18	52
SS-4	Raja Bazar	1860	39	56
SS-5	Chandni Chowk	1450	37	43
SS-6	Pirwaddahi	1680	38	57
SS-7	Committee Chowk	930	22	48
SS-8	Faizabad	870	39	22

*Averaged for 8:00, 12:00 and 16:00 hrs over 1-week sampling period for each site

Table 2. Typical meteorological parameters pertaining to day conditions at Sixth Road Chowk

Temp. (°C)	Relative Humidity (%)	Sunshine (Hours)	Wind Speed (km/hr)	Wind Direction	Pan Evaporation (mm/day)
35.2	38	7.2	4.1	E-W	8.5
28.8	67	5.9	3.4	S-N	3.5
30.0	67	7.7	3.2	E-W	7.4
26.2	78	4.8	3.5	S-N	2.2
29.0	67	9.5	2.4	E-W	4.0
28.8	70	11.1	4.2	S-N	7.1
29.8	66	12.1	1.8	S-N	7.3

The data revealed a divergent pattern of distribution of the metal concentration from site to site. The scrubbing method based Pb levels ranged from 18 $\mu g/m^3$ at site SS-3 to 39 $\mu g/m^3$ at sites SS-4 and SS-8. The observed increasing order of Pb concentration at various sites was: SS-3 < SS-7 < SS-2 < SS-1 < SS-5 < SS-6 = SS-8. An overall 10-15 % increase in Pb levels close to peak morning and afternoon hours was observed.

The data showed, in general, enhanced Pb levels at sites where traffic density was relatively higher. Traffic jams were normally avoided during sampling to disallow spurious estimates of Pb to enter the data-body. Such unrealistically high levels of Pb could only be seen to arise from a point source reflecting a build up of Pb due to an artificial stagnant condition, and thus not allowing for any natural dispersion of the metal in the atmosphere over the sampling time.

The Pb concentrations estimated by the high-volume sampling method appear in Table-1, (b), averaged over the entire period of one week of sampling at a specific site. Compared with the scrubbing method, the average Pb levels estimated by this method bear a strong positive correlation with r = 0.57, signifying that the sets of data are correlated at about 60 % level. This validates a straight forward use of the relatively non-time consuming scrubbing method toward predicting the levels of the metal prevalent on a given day and at a given time.

For the high volume sampling method (Table-1, b), the highest concentration of Pb (57 $\mu g/m^3$) was found for the site SS-6, a typically traffic congested location. The differences in the individual concentration of Pb determined by the two methods could be considered to arise from the time scale involved during sampling, together with varying conditions of traffic plying during the time when actual measurements were made, which of course could not be averaged. The study delineated an important feature of the scrubbing method that it could serve reliably as an instantaneous in-situ method compared with the high volume method, which calls for a prolonged 6-8 hr sampling time.

The climatic parameters reported in Table-2 are well known to have a bearing on the mass transport and dispersion of particulate matter in the atmosphere. For the present study, the temperature, sun-shine, wind speed and relative humidity parameters indicated a typical dry season during the sampling period. The relationship between airborne Pb concentration and average on-site temperature is shown in Fig. 2. Starting with the minimum temperature, 26.2 °C, the Pb concentration first decreased to 28.8 °C and then increased subsequently to 29.8 °C. This situation may be seen to be identical with respect to sunshine. The temperature parameter, therefore, exhibited no clear-cut relationship for the Pb levels distributed in the atmosphere, thereby showing a non-temperature dependence of Pb distribution in the local atmosphere. Wind velocity,

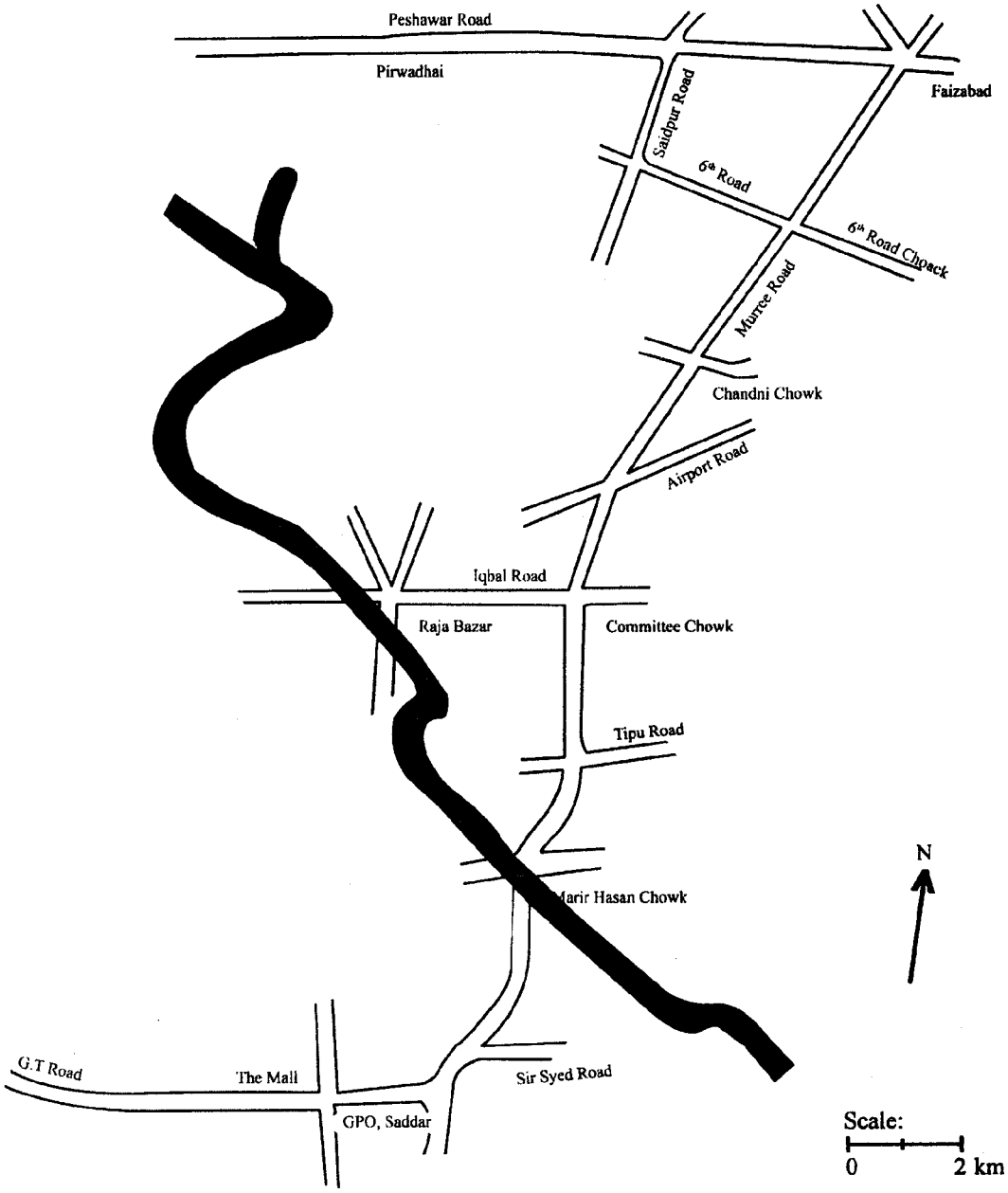

Fig. 1. Location map of sampling sites (*).

on the other hand, was seen to affect Pb distribution in a straight forward manner. The situation is shown in Fig. 3. Here, almost stagnant wind conditions are met; the wind speed varying between 1.4 km/ hr to 4.2 km/ hr has virtually no positive or negative correlation with Pb levels in the atmosphere. A similar situation is met in the case of relative humidity (Fig. 4), wherein both maximum and minimum concentrations of Pb were found to exist at about 66-67 % RH. The study thus revealed that the meteorological parameters do not obviously contribute critically toward the distribution of the

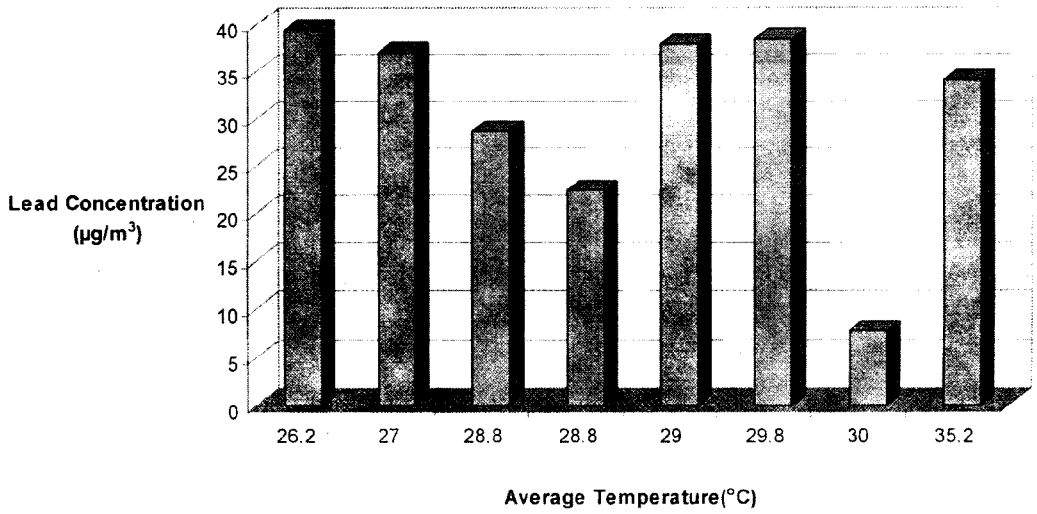

Fig. 2. Relationship between average Pb concentrations and average temperature.

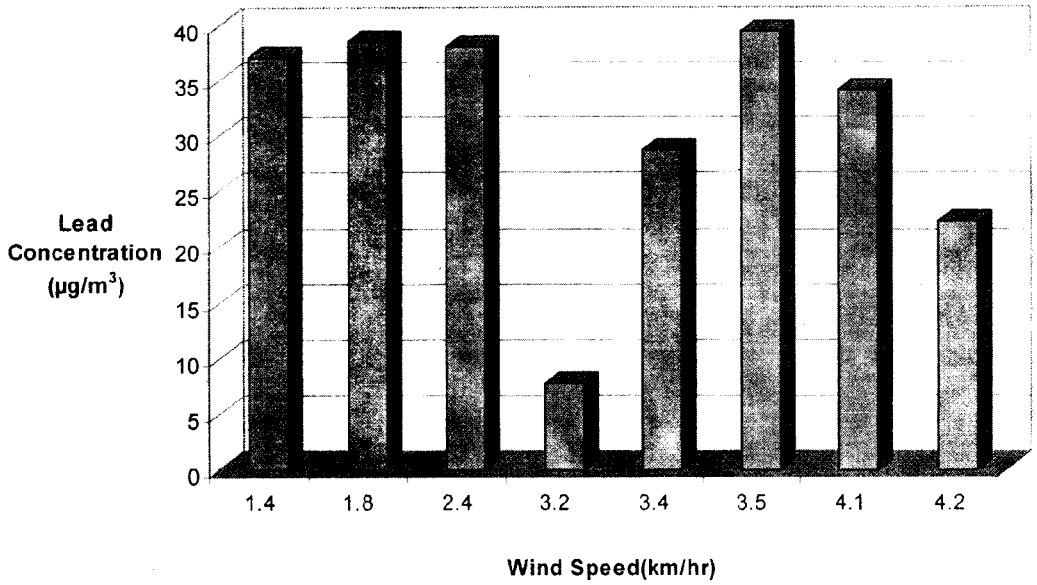

Fig. 3. Relationship between average Pb concentrations and wind speed.

metal, especially under the given conditions that all sampling sites were acting as point sources of pollution with a heavy pollutant load that cannot be evenly dispersed into the atmosphere as a function of time.

The present study brought forth the finding that the Pb levels determined presently are high by a factor of 7 to 10 as compared with those for counter-part environment in advanced countries. Compared with typical urban atmospheric Pb levels prevailing in other parts of the world, the current Pb levels were comparable with those reported for similar atmospheric environment. For example, Pb levels in Tai-wan were reported to range from 28 $\mu g/ m^3$ to 78.3 $\mu g/ m^3$ in a typical workplace atmosphere [14, 15]. Also, some data from Ho Chi Minh City reflected a range of 90 $\mu g/m^3$ to 179 $\mu g/m^3$ Pb for the

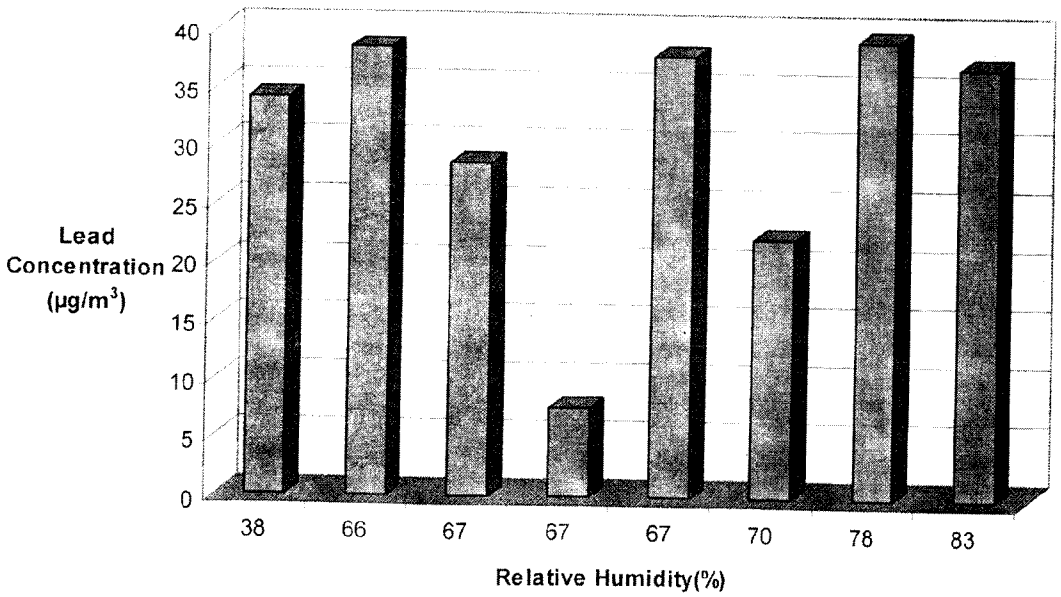

Fig. 4. Graphic representation of Pb concentrations vs. relative humidity.

suspended particulate matter [16]. In respirable fraction, a level of 50 $\mu g/m^3$ Pb had been reported with 150 $\mu g/m^3$ for the total Pb in dust [17]. However, for clean atmospheres without any probable Pb pollution, as low Pb concentrations as 0.244 $\mu g/m^3$ have also been reported [18, 19]. Also, the Pb concentration in local air was randomly influenced by weather conditions.

Experimental

Eight air sampling sites (Fig. 1), with widely varying traffic density, were selected. The sites were selected keeping in view the pattern of traffic density and the frequency of automobile operations in the typical urban routes of the city. The sampling times were fixed at 08:00, 12:00 and 16:00 hrs, for each day to ensure air sampling during the peak hours.

A LaMotte Air Sampler (Dwyer Instruments, USA) was used to trap particulate Pb from air in a scrubbing solution of dithizone in carbon tetrachloride-de, at a flow rate of 1.5 LPM. The concentration of the dithizone solution was 25 μmol/ L and 25 mL of this solution was sued in each run at the selected monitoring time. The scrubbing stock solution used in the present work was prepared by weighing 0.025 g of dithizone, dissolved in about 40 mL of pure carbon tetrachloride. The deep green solution was filtered into a separating funnel (250 mL capacity) and extracted with 25 mL of 0.075 M ammonia solution twice. The organic phase was discarded and the combined aqueous extracts were shaken with two 1 mL portions of carbon tetrachloride. Then, 50 mL of carbon tetrachloride was added and the solution was acidified with 2.5 mL of 0.5 M sulphuric acid with constant shaking. The organic phase was separated and washed with distilled water. This transfer of dithizone from carbon tetrachloride to ammonia solution and back again was repeated four times, till the extraction with ammonia solution left a practically colorless and clean organic phase. The dithizone solution was overlaid in a brown bottle with 2.5 mL of distilled water and 0.25 mL of 0.5 M sulphuric acid. The working solution was prepared by diluting 7 mL of the stock solution up to 500 mL with carbon tetrachloride. A scrubbing time of 20 minutes, equivalent to 30 L of sampled air, was employed for sampling at a specific time.

A High Volume Air Sampler (GMWL Handi-Vol 2000) was used to trap aerosol Pb on glass fiber filters (8"×10"), on 8-hourly basis daily, from 8:00 hrs to 16:00 hrs. The samples were digested subsequently in nitric acid (65 %, AAS grade), followed by treatment with 20 mL perchloric acid (36 %, AAS grade) to oxidize any remaining organic residue. The air flow rate was measured by a variable orifice meter, calibrated periodically to maintain on-

site accuracy. The digested samples so obtained were aspirated onto a Shimadzu AAS system, model AA-670. The standard calibration method was used for quantification of the metal under optimized analytical conditions given in Table-3. 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. All chemicals and reagents used were procured from E-Merck, with guaranteed 99.9 % purity.

Table 3. Optimum analytical conditions for the estimation of Pb on Shimadzu AA-670

Element	Pb
Wavelength	217.0 nm
Hollow cathode lamp current	7 mA
Slit width	0.3 nm
Flame	Air-C_2H_2
Fuel gas flow rate	1.8
1% Absorption concentration	0.2 ppm

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