Use of Hair as an Indicator of Environmental Lead Pollution: Changes after Twenty Years of Phasing Out Leaded Gasoline

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Abstract—Lead (Pb) poisoning is one of the most common and preventable environmental health problems. There are different sources of environmental pollution with lead as lead alkyl additives in petrol and manufacturing processes. Pb in the atmosphere can be deposited in urban soils and may then be re-suspended to re-enter the atmosphere. This could increase human exposure to Pb and cause long-term health effects. Thus, monitoring Pb pollution is considered one of the major tasks in controlling pollution. Scalp hair can be utilized for the determination of lead (Pb) concentration. It provides a lasting record of metal intakes of weeks or even months, and for most metals, their accumulation in hair reflects their accumulation in the whole body. This work was conducted to investigate the concentration of lead in male scalp hair of Cairo (residential-traffic and residential-industrial) and rural residents after twenty years of phasing out of leaded gasoline. Results indicated that the mean concentration of lead in hair of residential-traffic (9.7552 µg/g ±0.71) and residential-industrial (12.3288 µg/g ±1.13) was significantly higher than that in rural residents (4.7327 µg/g ±0.67). The mean concentration of lead in hair of resident’s industrial areas was the highest among Cairo residents and not the traffic areas as it was before phasing out of leaded gasoline. Twenty years of phasing out of leaded gasoline in Cairo has greatly improved the lead pollution among residents of traffic areas, but industrial areas residents were still suffering from lead pollution, which needs more efforts to control the sources of lead pollution.

Keywords—Heavy metals, lead, hair, biological sample, urban pollution, rural pollution.

I. INTRODUCTION

LEAD is a shiny, silver-colored metal found naturally in the earth’s crust. It has historically been used in a variety of products including paints, gasoline, batteries, bullets and some vinyl-products such as mini-blinds. Fine particles of processed or recycled lead and/or lead dust become a health hazard when they are taken into the body through inhalation (breathing) and/or ingestion (swallowing). So, lead poisoning is one of the most common and preventable environmental health problems today [1], [2]. Lead affects almost every organ and system in the body, especially the brain, central nervous system, kidneys, and immune system [3], [4]. Lead can also decrease calcium absorption in the body [5]. It is most harmful to young children under six years of age and especially to children less than three years of age due to their rapidly developing and immature body systems [6].

The tissue specimens of the body that can be utilized for the determination of lead (Pb) concentration are blood, urine, scalp hair, teeth, nails and internal organs. Of the six specimens, urine gives information of what the body has lost, not what is retained, generally not considered as a sensitive indicator for exposure [7]. Teeth are not readily available, very little are known about nails while internal organs are available only from autopsies. Hence blood and hair are the only two viable options the researcher is left with. As hair binds Pb at high concentrations and its growth is continuous, it gives a record of long term exposure [8]. Thus, blood Pb is a good marker for recent Pb exposure, while the determination of Pb in hair provides a lasting record of intakes of metal over weeks or even months [9]. For most metals their accumulation in hair reflects the accumulation in the whole body [10]. The Environmental Protection Agency (EPA) and the International Atomic Energy (IAEA) has recommended the use of hair as an important biological material for worldwide environmental monitoring [11].

Lead in the atmosphere can be deposited in urban soils [12] and may then be re-suspended to re-enter the atmosphere [13]. This could increase human exposure to Pb and cause long-term potential health effects [14]. Lead contributes more than 20% of the total mass of those fine particles emitted from burning of leaded gasoline, of which approximately 75% is emitted directly to the atmosphere [15]. Thus, monitoring Pb pollution has been one of the major tasks in controlling air pollution worldwide.

Tetraethyl lead was first introduced to anti-knocking gasoline additives in the 1920s, and Pb concentration in the atmosphere continually increased from that time, although it has declined dramatically from the last few decades, due to the phase-out of leaded gasoline. In California Pb concentration declined from 3000 ngm⁻³ in the early 1970s [16] to less than 10 ngm⁻³ [17] in 1990s. In China, the use of leaded gasoline was banned first in Beijing in 1997, and then in Shanghai, Guangzhou, Tianjin and other big cities. Wang et al. [18] evaluated the phase-out of leaded gasoline in Tianjin. They
found that Pb concentration of 1994–2001 decreased a little. The results indicated that the contributions from vehicles emission decreased, whereas those from other sources likely increased [19].

Air pollution in Cairo Metropolitan has been of concern for many years. Particulate matter is the most common air pollutant in urban and industrial areas. Lead was completely phased out from petrol distributed among Cairo, Alexandria, and most of the cities of Lower Egypt in late 1997, and consequently, lead concentration of the atmosphere of Cairo city centre and residential areas decreased markedly reaching less than 30% of those recorded during the early 1990s [20].

The aim of this work is to evaluate the levels of environmental contamination by Pb as indicated by measuring the Pb concentrations of human hair at different locations in Egypt and compare levels of lead in hair of residents since 22 years, before phasing out the leaded gasoline.

II. MATERIALS AND METHODS

A. Materials

1. Chemicals and Reagents

Stock standard solution (1000 mg/L) of lead (pb), acetone, absolute alcohol, H2O2, perchloric acid and redistilled concentrated nitric acid at high grade (BDH Chemical LTD) were purchased from Merck (Merck, Darmstadt, Germany). De-ionized water from Milli Q water purification was used.

2. Biological Hair Samples

Male scalp hair samples (180) were collected during the period of 1/5/2010 to 1/11/2012 from different districts in Cairo having different activities. These districts are heavy traffic residential area (Faysal), industrial residential area (Shoubra El-Kheima and Helwan) and rural area (near cultivated lands). Sixty hair samples were collected from each area. The collected hair samples were stored in clean polyethylene bags of 4°C during transportation. Once received, they had been frozen at -20°C until time for analysis. Each lot of collection bags, shipping, and storage containers are screened for lead contamination.

B. Methods and Procedures

1. Test Principle

Hair samples are digested by a mixture of HNO3 and H2O2 according to the method of [21]. The content of lead in digestion vessels is determined by atomic absorption spectrophotometer at maximum absorbance lamp.

2. Determination (Instrumentation)

Digested samples are measured for lead by PG-990 atomic absorption spectrophotometer (PG Instruments LTD) with flame atomization (air-acetylene), equipped with a 10 cm burner and a deuterium lamp for back ground correction. Maximum absorbance was obtained by adjusting the cathode lamp at wavelengths (217.0 nm). The other analytical parameters were; bandwidth, 0.4 nm; filter the factor, 1.0; lamp current, 5.0 ma; integration time, 3.0 sec; background, D2/SR and flame setting, oxidizing blue.

3. Method's Validity

a. Quality Assurance

Quality assurance procedures and precautions were carried out to ensure reliability of the results. All materials used for processing were screened for possible lead contamination. Acidic-clean volumetric flasks and other glassware was soaked in a soapy solution (2% solution isoclean detergent) for 24 hr., then rinsed and soaked in 10-15 % nitric acid for 48 hr., then rinsed with ultrapure water and dried under clean conditions. Deionized water was used throughout the study. The samples were generally carefully handled to avoid contamination.

b. Determination of Detection Limits

The detection limit is defined as the concentration which will produce an absorbance signal three times the standard deviation from the blank or the magnitude of the baseline noise. The baseline noise may be statistically quantities by making 10 or more replicate measurements of the baseline absorbance signal observed for an analytical blank, and determining the standard deviation of the measurements. According to this formula, detection limits was calculated and recorded which was 0.012 mg/L.

C. Statistical Analysis

The data obtained from this study was statistically subjected to analysis of variance (ANOVA) and means separation was by [22]. The least significant difference (L.S.D) value was used to determine significant differences between means and to separate means at p≤0.05 using SPSS package version 15.0. Data also were analyzed by SPSS® for Windows® ver. 20.0. Quantitative data was expressed as mean and standard deviation. Analysis of variance tests was used for comparison of means between three groups of variables; the test was significance when P value less than 0.05.

III. RESULTS

Hair samples of 180 males were collected from urban sites: residential-industrial, residential-traffic and rural sites during the period of 2010 to 2012. The concentration of lead in hair was determined and data reported in Table I. Results show that lead concentration in the hair samples of males from industrial areas of Cairo, ranged between 6.2847 to 19.0432 µg/g, with mean value of 12.3288 µg/g. On the other hand, lead content of hair samples of heavy traffic areas (residential-traffic areas) ranged between 2.8634 -16.3311 µg/g with mean value of 9.7552 µg/g. While lead concentration of the hair of male residents living in rural areas ranged between 1.0499-9.0402 µg/g with mean value of 4.7327 µg/g. Data proved that lead level in the samples are quite variable among the three areas. These results were confirmed by statistical analysis which highly significant differences (p≤0.05) was detected.
Comparing our results (2010-2012) with [23], data in Table III, showed that the mean concentration of lead in hair of rural areas and traffic areas in 2010-2012 were lower than those of 1990, and these decreases were statistically highly significant (p<0.0001). While the mean concentration of lead in hair samples collected from residential-industrial areas (12.388 \(\mu g/g\)) at years 2010-2012 was not statistically significant different with the mean concentrations of lead in the samples collection from the same areas at year 1990 (12.9 \(\mu g/g\)).

### IV. DISCUSSION

Sources of lead (Pb) in the atmosphere are either natural sources, which give to traces or very rare concentrations, or man-made sources. The biggest man-made source is batteries stores; the second man-made source is traffic and combustible fuels. The third big source is smelting and mostly coke, paints and pencils [20]. Although atmospheric lead originates from a number of industrial sources, leaded gasoline appears to be a principal source of general environmental Pb pollution. Tetraethyl lead was introduced as an anti-nock agent in gasoline in the 1920's [24] and since then has played an increasingly important role as a pollutant of the general atmosphere. Murozumi et al. [25], estimated that 90% of the atmospheric lead comes from automobile exhaust and that the increase in environmental Pb levels was due mainly to emissions from leaded gasoline.

The Government of Egypt introduced many efforts to reduce lead concentration of the environment. The Egyptian Environmental Affairs Agency (EEAA); has reduced significantly the lead content of gasoline sold in Cairo, where the Pb problem is most serious. After 1991 the tetraethyl lead as an additive agent was gradually reduced in gasoline sold in all the Cairo city stations. In 1996, unleaded gasoline was only sold in Cairo gasoline stations; but the leaded gasoline is still in use for other Egyptian governorates. And through five years plan i.e. at 1996; the gasoline sold was completely unleaded [26]. Consequently, the present study has been done to compare to lead in hair of Cairo residents and rural residents at 1990 and after unleaded the gasoline for more than twenty years.

Results presented in Table I shows that lead concentration in the hair of the male residents living in industrial and traffic areas in Cairo during years 2010-2012 has mean values higher than those detected in the hair of the male residents living in rural area during the same years. This in agreement with that of [23], who found that the concentrations of Pb in hair of Cairo population were significantly higher than those found in rural areas, which is attributed to the difference in the concentrations of that metal in the atmosphere of a megacity like Cairo, which is facing increased urbanization and industrialization [27], causing more increase in the level of pollutants than in the rural areas. Also, [28], [29] concluded that residents of urban/industrialized areas suffer more from increased Pb concentration in scalp hair than those of rural areas. The later study indicated that women living in the City of Karachi have approximately 600% higher Pb levels in their

### TABLE I

<table>
<thead>
<tr>
<th>Area of the samples collection</th>
<th>Concentrations ((\mu g/g)) ±SD</th>
<th>Mean ± SD</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial</td>
<td>12.3288±1.13 (60)*</td>
<td>6.2847-19.0432</td>
<td></td>
</tr>
<tr>
<td>Traffic</td>
<td>9.7552±0.71 (60)</td>
<td>2.8634-16.3311</td>
<td></td>
</tr>
<tr>
<td>Rural</td>
<td>4.7327±0.67 (60)</td>
<td>1.0499-9.0402</td>
<td></td>
</tr>
<tr>
<td>LSD at 5%</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All values are means of samples number determinations in each area ± standard deviation (SD).

Means within rows with different letters are significantly different (p<0.05).

(*) *Samples number in each area.

Data in Table II according to [23] shows that lead concentrations in hair of males from traffic areas in Cairo before phasing out of leaded gasoline, were in the range of 5-35 \(\mu g/g\) for an examined 118 samples with mean value of 13.7 \(\mu g/g\). This figure was significantly higher (p<0.001) than that recorded in the hair of rural men, where the detected mean concentration of the Pb in hair was only 5.5 \(\mu g/g\) with ranges of 2-15 \(\mu g/g\). On the other hand, mean Pb level in industrial areas was 12.9 \(\mu g/g\) with ranges of 4-27 \(\mu g/g\). Regarding to lead in scalp hair of Cairo population of [23] study, the highest concentrations of lead were recorded in the hair of those living in the residential- traffic areas followed by those living in the residential- industrial areas and rural areas.

### TABLE II

**LEAD CONCENTRATIONS (\(\mu g/g\)) IN SCALP HAIR OF ENVIRONMENTALLY EXPOSED MEN FOR THE YEAR 1990 IN EGYPT [23]**

<table>
<thead>
<tr>
<th>Living Areas</th>
<th>Pb concentration in hair ((\mu g/g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residential-Industrial areas N=40</td>
<td>Range 4-27</td>
</tr>
<tr>
<td>Residential-Traffic areas N=38</td>
<td>Range 5-35</td>
</tr>
<tr>
<td>Residential-Rural areas N=40</td>
<td>Range 2-15</td>
</tr>
</tbody>
</table>

*Highly significant than the other two areas.

### TABLE III

**COMPARISON BETWEEN LEAD CONCENTRATIONS (\(\mu g/g\)) IN SCALP HAIR (FROM NON-OCCUPATIONALLY EXPOSED) OF MEN AT THE YEAR 1990 AND YEARS 2010-2012 IN EGYPT**

<table>
<thead>
<tr>
<th>Living Areas</th>
<th>Lead concentrations ((\mu g/g)) in scalp hair of men</th>
<th>Year 1990</th>
<th>Years 2010-2012</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residential-Industrial areas N=40</td>
<td>Range 4-27</td>
<td>Mean ± SD 12.9± 5.8</td>
<td>6.2847-19.0432</td>
<td>0.000**</td>
</tr>
<tr>
<td>Residential-Traffic areas N=38</td>
<td>Range 5-35</td>
<td>Mean ± SD 13.7± 6.1</td>
<td>2.8634-16.3311</td>
<td>0.000**</td>
</tr>
<tr>
<td>Residential-Rural areas N=40</td>
<td>Range 2-15</td>
<td>Mean ± SD 5.5±3.1</td>
<td>1.0499-9.0402</td>
<td>0.16</td>
</tr>
</tbody>
</table>

*p-value <0.05 is not significant.

** P-value <0.0001 is highly significant.
hair than their age-matched counter parts living in rural environment in Bangladesh [29].

The highest concentrations of Pb were recorded in the hair of those living in the residential-industrial (12.3288 µg/g), which is higher than those living in the residential-traffic areas (9.7552 µg/g). Results presented in Table II show that lead concentration in the hair of the male residents living in industrial areas of Cairo at the year 1990 ranged between 4 to 27 µg/g with mean value of 12.9 µg/g. However, mean lead concentration of the hair samples of the male living in traffic areas ranged between 5-35 µg/g with mean value of 13.7 µg/g. On the other hand, the lowest levels of lead was detected in male hair samples collected from rural areas at the year 1990 which ranged between 2-15 µg/g with mean value of 5.5 µg/g.

The highest concentrations of lead were recorded in the hair of those living in the residential-traffic areas than those live in the residential-industrial areas. This is due to exposure to both groups to high level of leading in the air, where the Pb concentration of the atmosphere of residential-traffic areas (1.5gm³) was slightly higher than that measured in the residential-industrial (1.3 gm³). Ali and Nasralla [23] explained that by the fact that traffic areas were crowded with traffic activities as well as many metallurgical industrial processes emitting Pb particulate. The industrial areas were affected by the emissions of foundries and smelters located in the industrial districts of Imbaba and Shoubra-el-kheima [23].

The highly significant decrease from the level of Pb in hair of men living in residential-traffic areas in Cairo indicated that Pb pollution in the atmosphere of these areas has been decreased after phasing out of leaded gasoline. There is significant improvement in lead concentrations in the air where it reached 0.74 in 2008, while it was 1.67 µg/m³ in 2000 [30]. In the study carried out by [26], they concluded that the concentration of lead in ambient air of Cairo showed a notable decrease in that year after using unleaded gasoline. The mean annual decrease was 13% (per year). It is expected that this decrease will be much greater after using unleaded gasoline in all the governorates of Egypt. Also, Hassamein et al. [31] observed a decrease by 40% in the Pb concentration of urban areas of Greater Cairo. So, many author explained the significant decrease in atmospheric lead concentration of 1999 to 2002, by the efforts made to improve air quality especially lead emissions. These efforts included introduction to lead-free gasoline, beside the use of natural gas as fuel in houses and in some vehicles, also the underground metro as a long net in Cairo City, cleaning up of lead contaminating sources from the industrial areas by their relocation outside the residential blocks, as well as switching to the natural gas instead of mazout in the industrial areas and power generation sectors [32].

In China, the use of leaded gasoline was banned first in Beijing in 1997, then in Shanghai, Guangzhou, Tianjin and other big cities. The 5-year long-term programmer of Pb-monitoring from 2000 to 2004 was carried out at three representative urban sites (a traffic, an industrial, and a residential site), and a suburban site to evaluate the pollution level of Pb in Beijing. They found that Pb concentration has decreased a little [19]. The airborne Pb concentrations, in USA, Japan, and many countries in Europe, showed a major decrease in the phase-out of leaded gasoline since a longer period. In California Pb concentration declined from 3000 ngm⁻³ in the early 1970s [16] to less than 10 ngm⁻³ in 1990s [17]. The highly significant decrease in the Pb concentrations of hair of residents rural areas around Cairo follows the significant improvement in Pb concentrations in the air of Greater Cairo, in addition to lack of the rural areas for the dense traffic of Cairo, which may lead to more Pb emissions, from automobile exhaust coming from other governorates to the Cairo city [33]. As well as the findings of [34] on residence of Mansoura city confirm this meaning, where Pb concentration of the normal population of Mansoura was less than that in Cairo. Also the study of [32] found that, the lead concentration of the school ambient air of the urban area was 0.21 µg/m³; in the rural area, it was 0.14 µg/m³. Both of these values were below the maximum Egyptian limit defined in the executive regulation of the law number 4/1994, as being 1µg/m³ [35].

Finally, the Pb concentrations on hair of industrial areas don’t show any significant decrease, this could be explained by the pollution of air of Greater Cairo by: 750 Smelters, 530 Brick Factories, 1200 Metallurgical Factories, 12500 Industrial Facilties, 5 Thermal Power stations, 2 Oil Refineries and 19 Industrial Zones [36]. As, Greater Cairo according to the WHO classification is one of the largest mega cities in the world, a city upwards of 18 million inhabitants and is known as one of the most polluted cities in the world. Where, Cairo was the home to, one third of Egypt's population, 60 % of industries, 50% of electrical consumption and 48% of the countries motor vehicles. Zakey et al. [37] explained that in his study. Measures of pollutants in some places exceed internationally recognized standards and collective action organized around environmental issues is rare. The government is aware of these problems; environmental protection must be one of “Egypt's strong suit”.

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REFERENCES


Characteristics and sources of lead pollution after phasing out leaded gasoline.

