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Trace Metal Mercury Levels in Residential Homes in Kuwait

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Abstract: Kuwait is an oil rich state on the northeastern corner of Arabian Peninsula and has faced the unprecedented man made environmental disaster in early 1991 of igniting over 600 oil wells those continually burnt for a period of over six months. The use of crude and heavy fuel oil in the power generating facilities has aggravated the pollution due to particulate matters that carry trace metals. The climatic conditions in this part of the world result into very frequent dust storm transporting particulate matters short and long distance. Mercury in atmosphere is mainly due to burning of fossil fuel, incinerators, crematoriums, extraction of precious metals and salt-chlorine industries. This study has been initiated for mercury measurements from an old salt-chlorine industrial site that has been closed since 1984. To compare the mercury levels elsewhere, a comprehensive measurement program was devised and conducted to obtain mercury levels in most of the urban areas in Kuwait. Domestic dust samples from selected residences were collected for a period of a week. These samples were analyzed using KISR/T0-345 method especially developed for precise measurements of trace metals in particulate matter. It is required to identify the sources of mercury that resulted into such mercury levels in indoor air in the urban areas. For those areas where mercury levels are substantially high mitigation methods have been proposed to reduce the impact on to the residents.

Key words: Trace metal; indoor; particulate matter; mercury concentration; mercury species

INTRODUCTION

There is general consensus among internationally recognized scientists that annual mercury emissions have been increasing dramatically over last few decades. The major source is old aging coal fired power plants worldwide. The other dominant source is salt and chlorine industry that uses mercury cells for electrolysis of brine. The other point sources that contribute to the contamination of air, water and land are waste incinerators, flares, crematoriums and untreated wastewater.

In Kuwait city the major point source was a salt and chlorine plant, which was situated near Shuwaikh port using mercury electrode for the electrolysis of brine produced by neighboring Power and desalination plant. This industry was established in 1963 to relinquish growing need for chlorine for power/desalination plants and other municipal and household applications. In 1973 several new electrolytic cells were added to increase the production to 3865 tons of chlorine. In 1985, this plant was closed and dissembled. Another mercury free industry was commissioned at new location, Shuaiba to produce 9200 tons of chlorine with additional products, hydrochloric acid, caustic soda, and sodium hypochlorite. During the operation, it was estimated that 0.2 kg of metallic mercury was discharged per ton of chlorine produced that amounted 20 tons in this period[1]. High emissions due to harsh climatic conditions existing in this part of the world have been reported[2].

The other source that contributed to mercury deposition into Kuwait bay was discharge of tertiary treated wastewater and also some overflow of raw sewage from Ardyia wastewater treatment plant. Mercury pollution has been matter of concern and number of researchers has determined concentrations of mercury in water, sediments and biota in Kuwait Bay[3-6]. The probable sources, other than the mentioned above are oil flares, power stations and incinerators releases that contain mercury onto the total suspended particulates, TSP[7-10].

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Indigestion of dust and soil is widely regarded as the key pathway for childhood exposure to trace metal from paint, gasoline and other industrial emissions contaminants[11-17]. Pre-schoolers, especially older infants and toddlers spend most of their time indoor and ingest dust through normal repetitive hand-to-mouth activities[18-20]. The influence of low dose of mercury toxicity on human health mainly neurological, nephrological, immunological, cardiac, motor, reproductive and genetic disorder has been reported elsewhere[21]. Hood has summarized the effect of fish intake for pregnant mothers and discussed the merits of eating fish that is low in mercury but high in nutrients[22].

The present study focuses onto the measurement of mercury levels in the domestic dust collected from different residential areas in Kuwait, which determine exposures of toddler and pre-schooler older infants who spend most of their time indoor and ingest dust through normal repetitive hand-to-mouth activities.

METHODOLOGY

This method covers the determination of total mercury in sludge samples with detection limit of 1 μg kg^{-1} (1 ng g^{-1}). This method also can be applied to soil and sediment samples.

An aliquot of acidified sample is digestion using chemically generated chromate. This is known to breakdown all of the commonly occurring mercury species to mercury (II). Elemental mercury vapour is generated from the digestion sample by reduction with stannous chloride ($SnCl_2$) and is purged from solution by an argon carrier stream. The mercury vapours are detected by atomic fluorescence spectrometry. The procedure is automated by means of Avalon window software.

The linear dynamic range of this method is approximately 0.1ng kg^{-1} (0.1pg g^{-1}) to 100μg kg^{-1} (ng g^{-1}) when using continuous flow approach. Samples containing mercury at concentrations higher than the linear dynamic range may be analyzed following appropriate dilution of the sample.

The sensitivity of this method is dependent on the selected operating conditions. On maximum amplification each fluorescence arbitrary unit is equivalent to approximately o.1ng. The method detection limit (MDL) will be dependent on the selected operating conditions and calibration range. With high purity reagents a MDL of less than 0.1ng kg^{-1} (0.1pg g^{-1}) is obtainable. The relative standard deviation is typically less than 5% for concentration greater than twenty times the method detection limit. The chromination digestion procedure coupled to atomic fluorescence spectroscopy overcomes much interference. The chromination overcomes interferences of mercury complexes with organic materials. Chloride interferences is also overcome. Suppression effects resulting from quenching of fluorescence signal may be encountered. Dissolved gases species are normally removed during the digestion stage.

Reagents:

1. Nanopure deionized water used in preparation of all solutions
2. Mercury standard 0.5, 1 and 2 mg dm^{-3} are prepared from 100mg dm^{-3} stock solution from (BDH in 0.5N HCl).
3. 33% v/v Hydrochloric acid (HCl)
   Dilute 167 cm^3 of high purity 36% v/v hydrochloric acid (HCl) to 500 cm^3 with water.
4. High purity potassium dichromate $K_2Cr_2O_7$)
   Dissolve 10g of $K_2Cr_2O_7$ in 100 cm^3 of water.
5. 2% stannous chloride ($SnCl_2$) solution
   Add 20g of $SnCl_2$ to 334 cm^3 of 33% v/v HCl and heat to dissolve. Dilute it to 1 dm^3.

Reagent Blank : Prepare a solution containing 150 cm^3 of 33% v/v HCl to 1 dm^3 by adding water.

It is important to use high purity reagent in all cases. The concentration blank value should have mercury less than 0.1μg kg^{-1}.

Apparatus: Atomic Fluorescence System-Millennium Merlin PSA 10.025. An argon gas supply (high purity grade 99.99%). Laboratory-ware: For the determination of mercury at very low concentration, contamination and loss are of critical consideration.

Procedure:

1. Instrument Parameters:
   The instrument parameters for mercury are:

- Wave length 273.5nm
- Instrument mode Fluorescence
- Calibration mode Concentration
- Sample introduction Manual
- Background correction off
- Argon gas pressure 300 k Pa
- Sample flow rate $8cm^3min^{-1}$
- Acid channel 7M HCl
- Replicates 3

Calibration:
Setup the programme in the computer microprocessor Avalon for the standard to be used in calibration and sample for the analysis. Run blank, 1 and 2 μg dm^{-3} standards in triplicate and obtain calibration curve. Run standard (e.g. 0.5) as sample and check the concentration obtained with RSD%, if satisfactory proceed with analysis of sample.

Sample Preparation:

- Dry the sludge samples in a dryer
- Grind and dry the sample at room temperature for eight hours and store in a desiccators.
- Take about 10 g of dried sample in a beaker
- Add 40 cm^3 concentrated hydrochloric acid (con. HCl)
- Heat at 80°C over a water bath with beaker covered with watch glass.
- Cool down then add 5 cm^3 of $K_2Cr_2O_7$ solution.
- The sediment and soil sample is similarly prepared and digested as that of sludge but the insoluble portion is filtered before the analysis.
- Collect sample in 10 cm^3 volumetric flask and fill up to the mark with deionized water.

Sample Analysis: Run the sample immediately after standards and record the concentration of mercury as μg kg^{-1} (ng g^{-1}).

Calculations: The concentration of mercury in the sample is automatically calculated by the built in microprocessor from the standard calibration curve.

Precision and Accuracy:
The precision of method for laboratory made standard is 1.0±0.1μg dm^{-3} for mercury.

SAMPLING AND ANALYSIS

Kuwait has high frequency of dust storm other than dust generated by human activities. PM_{10} measurements and total dusty events in Kuwait have been discussed in detail[23] that showed the highest annual average concentration in year 1997 exceeding 326μg m^{-3}. The maximum weekly PM_{10} concentration recorded was in the month of May 721.1μg m^{-3}. Dust samples were collected from residential houses. A new bag was installed in vacuum cleaner and dust was collected for one week using this particular appliance. The dust was separated and sieved to obtain a representative sample of PM_{10} that was digested and above procedure was followed with the best quality control and quality assurance. The maximum weekly mean values for the month of January to July[23] are used to convert mercury concentrations from dust sample (ng g^{-1}) to ambient air (ng m^{-3}) and compared with reported values for the other part of the world.
The cold vapour technique was used for accurate determination of mercury in dust samples. The instrument was daily calibrated using Mercuric sulphate analytical grade supplied by Merck Chemicals and standard solutions of 5ppb, 10ppb and 50ppb were prepared and linearity of the calibration has been regularly tested.

RESULTS AND DISCUSSION

Kuwait inherits hot and arid climate due to its location in the tropical region and all residential, commercial, industrial and institutional buildings are served by air-conditioning. People spend most of their time in indoor environment, thus making it crucial for comfort, health and productivity. Outdoor pollutants mainly from traffic, power stations and industrial activities can penetrate into indoor residential, offices, commercial and governmental buildings that are more airtight than the older structures due to high-energy efficiency. Indoor pollutants emanate from a range of sources: combustion products from cooking, volatile organics from paints, adhesives, cosmetics, insecticide, fresheners, furniture, carpets, wall papers and other building materials etc and flux of outdoor pollutants with fresh air draft. There is an increasing concern over the effect of IAQ on health of the occupants as ingestion of dust is widely regarded as the key pathway for childhood exposure to trace metal and metalloids. Pacyna et al.,[24] have discussed anthropogenic emissions of mercury worldwide for year 1995. The main sources are aging power plants, petroleum related industrial complexes, wastewater treatment units, incinerators and crematoriums etc. Orihel et al.,[25] have studied the fate of mercury, using isotopes to trace mercury from inorganic state to methyl mercury in 3 to 8 weeks time.

Six different clusters of areas in Kuwait were selected and sampled for domestic dust during the December 2005 to April 2006, Figure 1. The concentration of mercury varied from coastal area to inland as shown in Figure 1. The highest concentration was near to coastal area that had reminisced of old salt-chlorine plant that used mercury cells for electrolysis that is similar to the reported results elsewhere[26].The second highest concentration was in Jahra proximity to the northern oilfields depicting flaring activities. The third highest concentration was near Shuaiba industrial area consisting of petroleum refineries, and petrochemical complex.
There were 12 samples taken from Jahra residential area (one of the oldest inhibited area in Kuwait) and

mercury concentration in domestic dust was reported 664±σ ng/g or (μg/kg) where σ was about 1025.

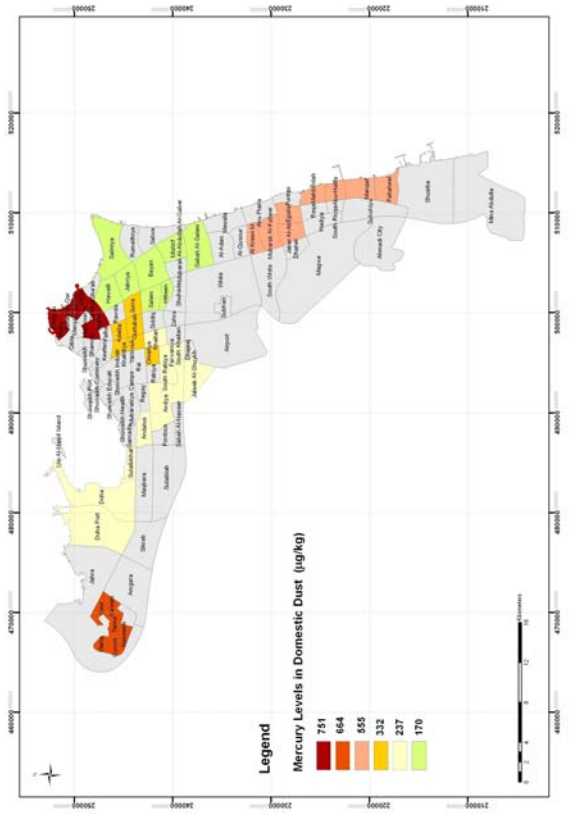

Fig 1: Mercury concentration in domestic dust samples collected from different residential area in Kuwait

Figure 2 shows the variation of mercury in Jahra area. One third of the total samples taken have shown very low concentration of mercury in domestic dust while others had significant high mercury concentrations.

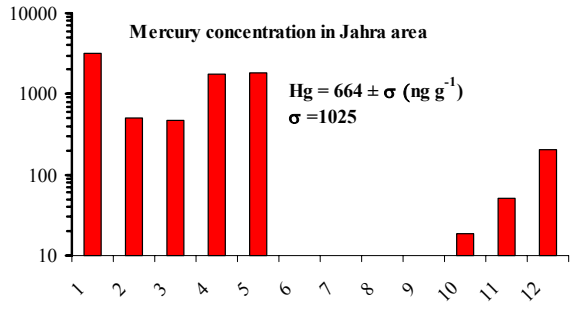

Fig. 2: Mercury variation in domestic dust samples in Jahra urban area.

Thirteen samples were collected from Mubarak Al-Kabeer residential area and mercury concentration is 555±σ ng/g or (μg/kg) where σ is about 1115 as shown in Figure 3. This area is relatively new development and had a history of domestic waste dump. Mercury concentrations varied from sample to sample depending on the location of the house, vicinity to the petroleum refineries and petrochemical industries that excessively use flares to get rid of gaseous, liquid and solid waste.

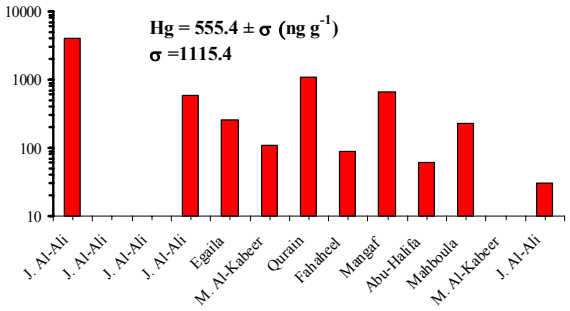

Fig. 3: Mercury variation in domestic dust samples in Mubarak Al-Kabeer area.

About eight samples were obtained from coastal Kuwait Bay residential area substantially old and mercury concentration was found to be 751±σ ng/g or (μg/kg) where σ was about 1106 as shown in Figure 4. There was random variation from sample to sample depending on its location and proximity to the Kuwait Bay which is contaminated as reported in literature[3-6]. The other urban residential areas were selected deep inland away from the contaminated Kuwait Bay.

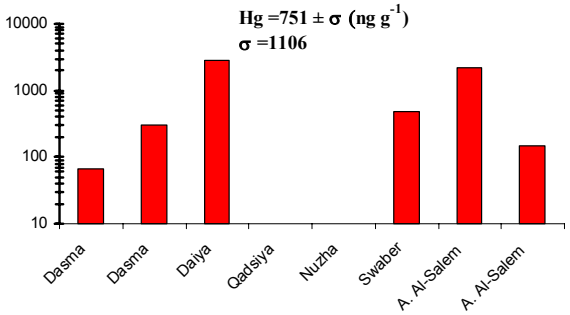

Fig. 4: Mercury variation in domestic dust samples in urban area near to the coast.

Two central residential areas, where nine and fourteen samples of domestic dust were taken and analyzed, had mercury concentrations 237±σ and 322±σ ng/g (μg/kg) and were shown in Figures 5 and 6.

Table 1: Average concentrations of gaseous elemental mercury in the major cities in the world

Area	Country	City	Exp. year	Average (ng m^{-3})	Standard deviation	Reference
Asia	Present	Jahra		2.28		Present study
		M. Al-Kabir	2006	3.0		
		Coastal area		2.02		
	China	Beijing	1998	8.3-24.7	13.1-24.8	Liu et al.,[27]
		Changchun	1999-00	18.4		Fang et al.,[28]
		Guiyang	2001-02	8.4		Fang el al.,[29]
	Korea	Soul	1987-88	14.4	9.56	Kim & Kim[30]
		Soul	1999-00	5.34	3.92	Kim & Kim[30]
	Japan	Tokyo	2000-01	2.7	3.59	Skata & Marumoto[31]
Europe	France	Bordeaux	1995-96	2.7		Pecheyran et al., [32]
North America	USA	4 sites in Connecticut	1997-99	2.19-2.69	0.66-1.72	Nadim et al.,[33]
		Broward County	1993	2.8-3.3		Dvonch et al.,[34]
		Chicago	1994-95	3.6	2.9	Landis et al., [35]
		Detroit	1999-02	1.17-40.33		Lynam & Keeler[36]
		New York	2000	3.84		Carpi & Chen[37]
	Canada	Toronto	2001-02	2.48	2.22	Denis et al., [38]

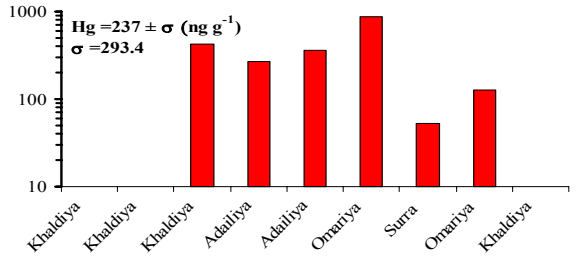

Fig. 5: Mercury variation in domestic dust samples in urban area

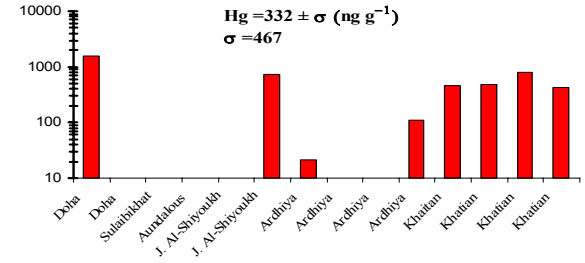

Fig. 6: Mercury variation in domestic dust samples in residential area

The standard deviation values σ were 293.4 and 467 respectively. There were lower mercury concentrations in domestic dust samples due to adequate dispersion from distant sources, power plants, oilfield, gathering center and petroleum industries flares.

Other samples were obtained from residential area near the Arabian Gulf coast and adjacent newly build areas. Mercury concentration was found to be 170.3±σ ng/g or (μg/kg) where σ was about 289.3 as shown in Figure 7. These mercury concentrations were the least measured values among all the residential areas cluster considered in Kuwait.

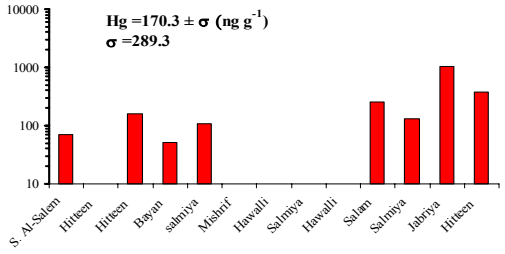

Fig. 7: Mercury variation in domestic dust samples in residential area

To compare with other cities in the world the detailed results have been tabulated in Table 1. The variation in the results is due to anthropogenic sources existing in different countries at the sampling sites that resulted into large value of standard deviation.

There is a strong influence of seasonal variation as in Kuwait there is a very strong predominantly northwestern wind throughout the summer season. These strong winds cause dust storm with high frequency effecting the ambient air concentration of various contaminants

It is not easy to compare mercury in particulate matter with mercury measurements in ambient air in different cities in the world. The average value of mercury in domestic dust from Kuwait is, in most cases, higher than those from mercury concentrations in the ambient air in other urban cities in Asia. Data from Asian area, especially from China, are significantly higher. It is good to see the decrease of mercury in some Asian areas, such as Seoul, during the last decade (Table 1). NuBlein et al.[26] have reported that indoor mercury pollution varied over a wide range due to individual hygienic state of the homes (housekeeping, ventilation and humidity). The mercury contents in the soil of home gardens showed no correlation to the gaseous as well as particulate mercury determined in the air of the adjacent rooms.

Intensive research programs are in progress across Europe to determine the distribution of mercury species across Europe. Very limited data, however, are reported on mercury concentrations in urban environment in Europe. The present findings show that the mercury in particulate phase in the urban atmosphere is characterized by high standard deviations. As discussed above, this statistical parameter basically shows the effects from human activities rather than poor reproducibility of the analytical instrument thus can be considered as a unique characteristic of urban atmospheric mercury concentrations water.

CONCLUSION

The result of the present limited study revealed that the concentrations of mercury in particulate matter in the urban residential atmosphere in the coastal areas in Kuwait are elevated, compared with those from inland areas and newly built areas. The Kuwait Bay has an eminence of a salt-chlorine factory that used mercury electrolytic cells and has contaminated the whole bay. Arabian Gulf on the contrary has not that high concentration of mercury in the sediments. The concentrations are highly variable, due to anthropogenic emission, canopy and urban, and temperature effects. Future studies are required to identify the sources of emission thus to develop emission control strategies. Information on mercury species, gaseous elemental mercury, reactive form of mercury and particulate mercury in the urban atmosphere is needed to assess the transport, transformation, deposition, and health effect of mercury.

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