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Environmental monitoring of mercury in urban soils, air and plants of a Mediterranean area, Alexandria, Egypt

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Abstract
This study was conducted in order to assess the levels of mercury (Hg) in air, soil, and plants in an area around chlor-alkali plant using mercury cells to produce chlorine gas. The output results indicated that the levels of Hg were decreased in the studied components with increasing the distance from the hot spot. Geographically, the highest levels of Hg were recorded to the prevailing wind direction i.e., Southeast direction, while the other directions West and East had the lowest levels. A wide variation in the amount of total Hg in the air samples collected at different distances around the hot spot was found. Also there was a pronounced difference in Hg concentration in soil samples depending on location and sampling time. The maximum concentrations of soil Hg were measured during February 2008 for all sampling directions. The levels of total Hg in plant samples during the period of 12 month-study were relatively narrow compared with the levels in air and soil which represented great differences in the total Hg among different directions and sites.

Keywords: Air; Environmental pollution; Mercury; Plant; Soil.

1. Introduction

Environmental pollution by mercury (Hg) has a great concern due to its potential as a neurotoxin [1]. This nonessential element has been listed as one of the priority pollutants by many international agencies, such as United Nations Environment Programme, World Health Organization and Food and Agriculture Organization of the United Nations, due to its possible toxicity to living organisms [2]. Although mercury is naturally occurring in soil depending on the soil type and its parent material at levels generally not exceed 0.1 mg kg^{-1} [3], human activities may contribute to enrichment of Hg concentrations in certain areas of the world. Coal burning, municipal solid waste incineration [4], electronics, paper, and pharmaceutical industries were identified as the major sources of anthropogenic emission of Hg [5]. Hg Emissions from chlor-alkali plants have been reported to have significant impacts on the environment [4]. The literature shows that once emitted to the atmosphere Hg may be transported over long distances [4, 6-8] and that due to the combination of its volatility and its chemical persistence, Hg tends to participate in global air–soil exchange processes [9]. Direct dry deposition of Hg to plants has also been observed [10-13], and uptake of only a small percentage of the atmospheric Hg by plants could substantively impact the input of mercury to terrestrial ecosystems. In order to effectively model

the residence time of Hg in the atmosphere, its removal processes and kinetics from the atmosphere must be well understood [14].
The present study was focused on the environmental monitoring of Hg in the urban soils, air and plants from an industrial area in Alexandria city, Egypt. Total Hg levels in the study area were compared to concentrations in literature for other urban areas. The objective of this study was to assess the levels of mercury in the above mentioned environmental compartments around an area includes some industries addressed as sources for Hg vapors.

2. Material and methods

2.1 Study area

The study area is located to the western sector of Alexandria city (Figure 1). It represents a complex industrial center (oil refining, petrochemicals, cement production and chemical industries). Of special interest is the Misr Chemical Industries Company (MCIC), chlor-alkali plant. This plant used the mercury cells in the production of chlorine and soda lime and therefore it is considered the main source of mercury in Wadi Al-Qamar area, which is located at Al-Max industrial region to the west district of Alexandria governorate. Wadi Al-Qamar has a net area of about 44 acres (185,000 m^2) (Figure 2).

2.2 Sampling procedures

Air, soil, and plant samples were collected from 8 sites in different directions and distances from the hot spot of mercury emission source i.e., MCIC. The sampling locations, in general were selected to represent sites around the hot spot to Southeast and West directions, and at different distances, taking into consideration wind direction in each area (Figure 3). The samples of air, soil and plant were collected for 12 months (Nov. 2007 to Oct. 2008) at prevailing and non prevailing wind directions.

2.3 Air sampling

A standard method [15] was used for the collection of mercury, from ambient air in the vapor phase. This method involves use of gold coated bead traps and glass-fiber filters. The sampling process for vapor-phase mercury requires a flow rate low enough to allow adsorption of the mercury in the air to the gold surface.
In this work Vapor-phase Hg is collected using gold-coated glass bead traps. A Teflon filter pack with a glass fiber filter is placed in front of the traps to remove particulate material from the air being sampled. Air is pulled through the vapor-phase sampling system using a mass-flow controlled vacuum pump at a nominal flow rate of 0.3 L min^{-1}. Determination of Hg in the collected samples is accomplished using cold-vapor atomic fluorescence spectrometry (CVAFS). The sample trap is heated to release the collected mercury. The desorbed mercury is carried in an inert gas stream (Ar) to a second gold-coated bead trap, the analytical trap. The mercury collected on the analytical trap is then thermally desorbed and carried into the CVAFS analyzer. The resulting voltage peak is integrated to produce peak area for the sample from which the concentration of Hg produced in μg Hg m^{-3} air. It must be considered that air samples for total mercury measurement were carried out at 1.5 meter above the ground surface [16].

2.4 Soil sampling

Soil Samples were collected at different distances from the hot spot (Figure 3). Moreover; the samples were collected at 1-10 cm depth of the superficial layer of soil from the different sites. The samples were collected in polyethylene bags, air dried, crushed by a round wooden lump and the shell fragments (when present) were removed away. The soil was then finely ground in a mortar and stored for chemical analysis.

2.5 Plant samples

The wild plant samples were collected from the same sites of air and soil samples (Figure 3). The dominant wild plant in Al-Max area was *Nerium oleander*. The plant leaves were placed in paper bags, dried in oven at 35 °C for 24 h, crushed by hand finely and stored in a glass desiccator for Hg analysis.

2.6 Determination of Hg in soil and plant samples

Determination of Hg in soil and plant samples required acid extraction prior to analysis [15]. The samples are extracted in a nitric acid solution using microwave digestion to yield "acid extractable" mercury. The extract was oxidized with BrCl to convert all forms of Hg to Hg^{+2} and $SnCl_2$ was added to the extract for

the reduction of Hg^{+2} to volatile Hg^{o}. The Hg^{o} is liberated from the extract by purging with an inert gas (N_2) and collected on a gold-coated bead trap. The amount of mercury collected on the trap is then determined using CVAFS.

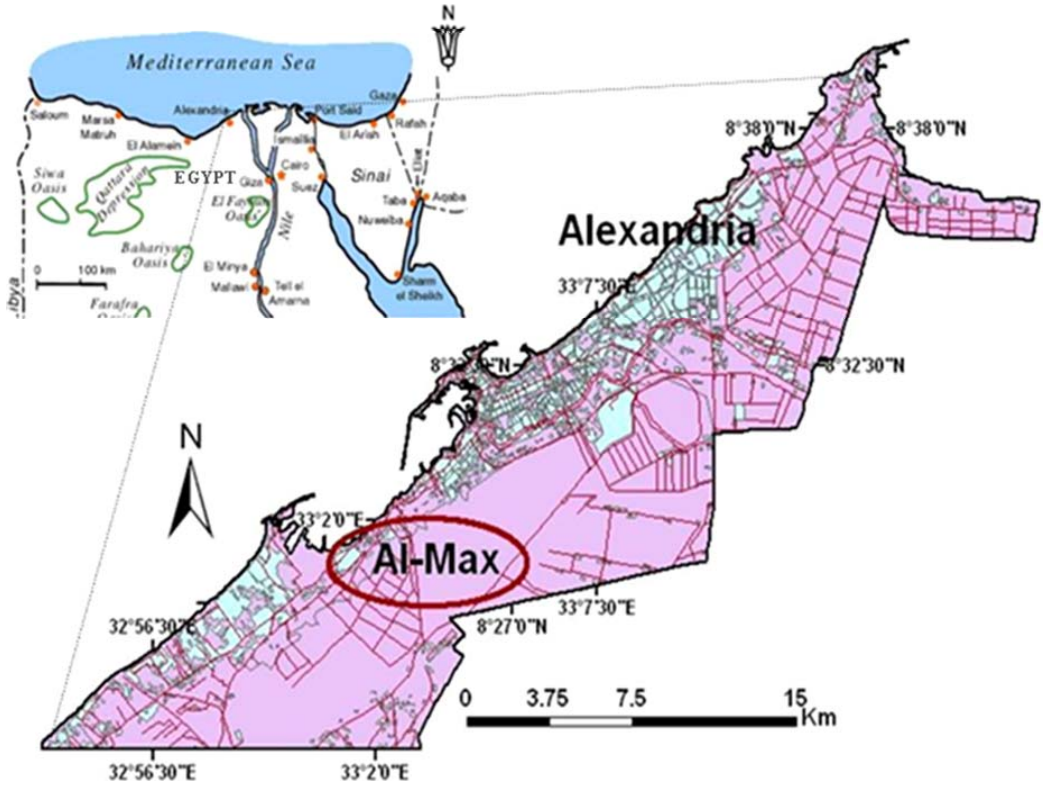

Figure 1. Location of study area in Al-Max region to the western district of Alexandria

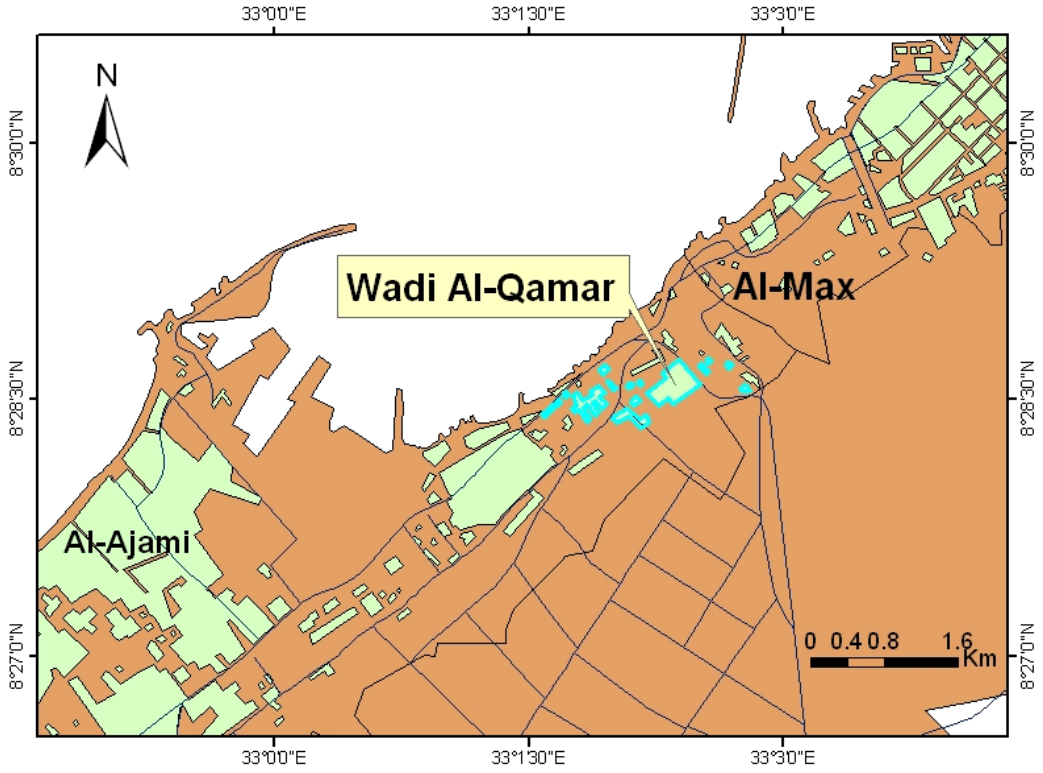

Figure 2. Al-Max industrial zone and the affected area of Wadi Al-Qamar

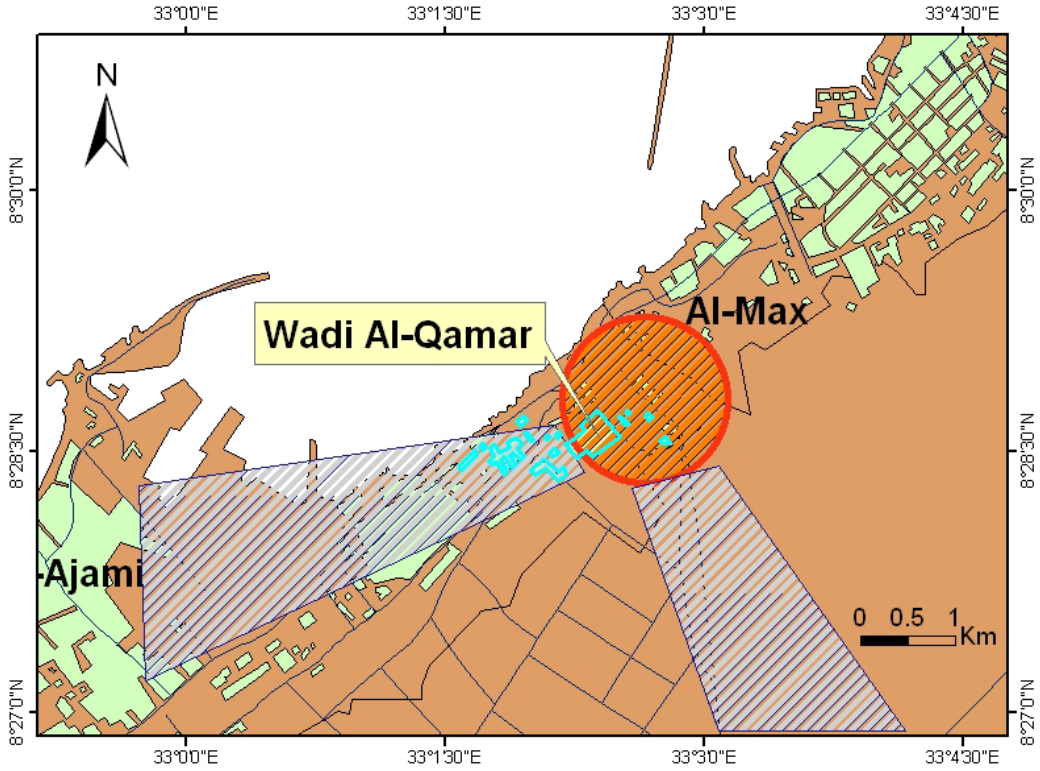

Figure 3. The sampling directions (gray shaded) from the hot spot area (red shaded)

3. Results and discussion

3.1 Mercury in air

The total levels of mercury in air were measured at eight sites representing the three directions Southeast, East and West around MCIC as shown in Figure 3. The results in Table 1 showed that there were differences in total mercury levels in air with sampling directions. A wide variation in the amount of total Hg in the air samples collected at different distances around the hot spot was found. This variation in the levels of Hg-vapor among the different sites might be attributed to both wind direction and distance from the hot spot. According to the meteorological data [17], the prevailing wind direction in Al-Max area is about 50% from the North West direction as illustrated in the wind rose Figure 4. This would enhancing the transport of Hg vapors from the hot spot to a longer distance along the South east direction than the other two directions, East and West, which had the least frequencies blowing wind.

As presented in Table 1 according to the dominant wind direction, high proportion of Hg vapors have been transported along the Southeast direction at the start point 0.5 km, 1 km and 2 km away from the hot spot relative to other sites which were located parallel to the East and West directions. Therefore, there are three main factors that may affect the concentration of mercury in air; (i) the sampling date (seasonal variation), (ii) the wind direction (Figure 4), and (iii) the sampling distance. Similar results were obtained [18] in which mercury concentrations in the atmosphere were depending greatly on the wind direction. On the other hand, it was stated that the total distribution of mercury in air is depending on wind direction [19]. Then mercury in Al-Max could be transported over 10 km from the hot spot along with the dominant wind direction [20]. The third factor i.e, the sampling distance, as the distance increases from the hot spot, the level of Hg decreases and this relationship appears clearly in the eight sites along twelve months. It was found that, large Hg concentration in air occurred within 1.6-3.2 km from the copper smelter source and decreased with increasing distance to a maximum of 8 km [21]. In addition another study revealed Shalaby [22] that the highest levels of Hg in air were observed close to the hot spot and these levels gradually decreased with increasing distance away from the hot spot.

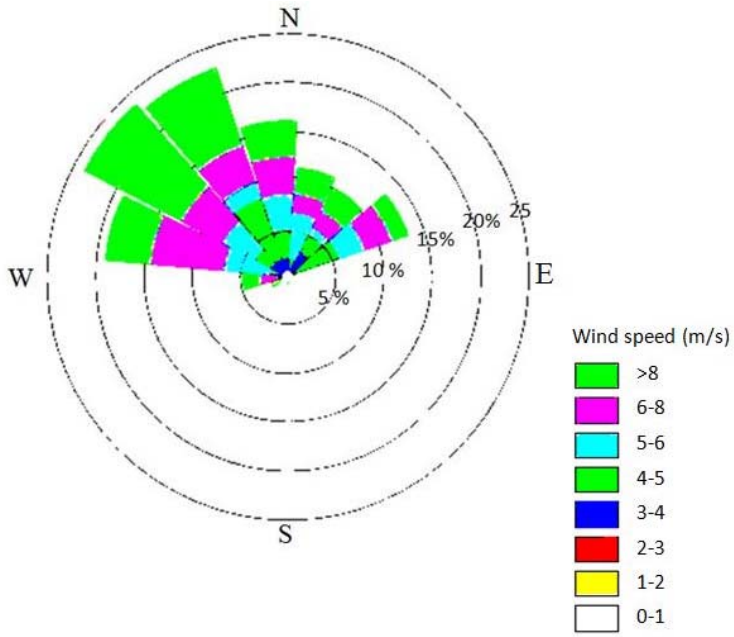

Figure 4. Wind roses representing one year in Alexandria city, Egypt

Table 1. Average, minimum and maximum concentrations of total Hg in air (µg m^{-3}) in different directions at different distances from the hot spot. Air samples collected from Al-Max area in Alexandria city during the study period (Nov. 2007 - Oct. 2008)

Variable	Southeast			East			West	
	0.5 km	1km	2 km	0.5 k	1 km	2 km	1km	2 km
Samples number/site	12	12	12	12	12	12	12	12
Average Conc. µg m^{-3}	40.3	34.2	32.42	24.84	24.88	19.48	20.9	12.9
Standard deviation	17.4	15.21	16.08	14.26	9.54	6.95	7.16	5.0
Minimum Conc. µg m^{-3}	16.5	14.28	12.8	10.58	12.8	10.1	11.2	7.9
Maximum Conc. µg m^{-3}	69.5	59.6	60.0	53.5	43.1	31.9	35.8	26.2

3.2 Mercury in soil

In the present study, the total Hg concentration in the soil samples was measured at sites representing the three directions around the chlor-alkali plant during the period from Nov. 2007 - Oct. 2008. The results showed a great difference in Hg concentration in soil samples depending on location and sampling time as shown in Table 2. Regarding to the levels of soil Hg at the nearest point to the hot spot (0.5 km) to the dominant wind direction (Southeast), it was found that the maximum content of soil Hg 2.43 µg g^{-1} was measured in February 2008, while the minimum soil Hg content was found to be 1.75 µg g^{-1} in May and June 2008. In comparison with the farthest sampling point (2 km) in the same direction the maximum concentration of soil Hg 2.03 µg g^{-1} was also recorded in February 2008, while the minimum concentration that recoded in May 2008 was 1.26 µg Hg g^{-1} soil.

As presented in Table 3 the highest average Hg level in soil was 1.92 µg g^{-1} at the nearest distance (0.5 km) to the hot spot to the Southeast direction, while the lowest average was 0.27 µg g^{-1} at 2 km away from the hot spot to the West direction. The results showed a slight increase in the levels of soil Hg in winter season than in summer. There was no significant difference between Hg levels along the eight sampling sites through the winter and summer seasons as shown in Table 4. This could be attributed to the fact that atmospheric deposition of mercury (dry and wet deposition) was more pronounced in winter season than in summer (i.e. Hg in soil increased at low temperature). It was stated that the magnitude of mercury loss increases as the soil temperature increases from 16 to 35°C [23]. Another investigation [24] demonstrated that the release of Hg° (volatile form) from the soil was parallel to the vaporization curve for Hg°, suggesting that evaporation was the primary process controlling soil Hg evolution.

Table 2 . Levels of total Hg in the soil samples (µg g^{-1}) at different sites around MCIC from Al-Max area of Alexandria City during the study period (Nov. 2007 - Oct. 2008)

Directions	Distance to the hot spot	Months Nov. 2007- Oct. 2008											
		Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.
		Hg (µg g^{-1})											
Southeast	0.5 km	2.05	1.99	2.0	2.43	1.99	1.80	1.75	1.75	1.78	1.82	1.89	1.92
Southeast	1 km	1.98	1.76	1.88	2.10	1.72	1.60	1.56	1.56	1.60	1.69	1.72	1.78
Southeast	2 km	1.51	1.57	1.68	2.03	1.47	1.31	1.26	1.32	1.39	1.44	1.52	1.61
East	0.5 km	1.12	1.21	1.25	1.58	1.08	1.00	0.89	0.93	1.02	1.14	1.21	1.34
East	1 km	1.28	1.19	1.39	1.46	0.89	1.01	1.10	1.01	1.08	1.14	1.17	1.23
East	2 km	0.92	0.84	0.95	0.98	0.69	0.71	0.70	0.71	0.80	0.91	0.99	1.03
West	1 km	0.56	0.44	0.43	0.49	0.33	0.48	0.48	0.49	0.48	0.51	0.57	0.58
West	2 km	0.26	0.29	0.3	0.20	0.28	0.23	0.28	0.29	0.25	0.28	0.28	0.32

Table 3. Average, minimum and maximum of total Hg concentrations in soil samples collected from Al-Max area, Alexandria city during the study period (Nov. 2007 - Oct. 2008)

Variable	Southeast			East			West	
	0.5 km	1km	2 km	0.5 km	1 km	2 km	1km	2 km
Samples number/site	12	12	12	12	12	12	12	12
Average Conc. µg g^{-1}	1.92	1.73	1.48	1.12	1.14	0.81	0.48	0.27
Standard deviation	0.19	0.17	0.21	0.18	0.17	0.12	0.07	0.03
Minimum Conc. µg g^{-1}	1.75	1.56	1.26	0.89	0.89	0.63	0.33	0.20
Maximum Conc. µg g^{-1}	2.05	1.98	2.03	1.58	1.46	0.98	0.58	0.32

Table 4. Levels and averages of total Hg concentration in soil (µg g^{-1}) at the sampling sites around the hot spot during summer and winter seasons at Al-Max area, Alexandria city

Directions	Distance to the hot spot	Winter 2007			Summer 2008		
		Dec.	Jan.	Feb.	June	July	Aug.
		Hg (µg g^{-1})					
Southeast	0.5 km	1.99	2.00	2.43	1.75	1.78	1.89
Southeast	1 km	1.76	1.88	2.10	1.56	1.60	1.69
Southeast	2 km	1.57	1.68	2.03	1.32	1.39	1.40
East	0.5 km	1.21	1.25	1.58	0.93	1.02	1.14
East	1 km	1.19	1.39	1.46	1.01	1.08	1.14
East	2 km	0.84	0.95	0.98	0.71	0.80	0.91
West	1 km	0.44	0.43	0.49	0.49	0.482	0.50
West	2 km	0.29	0.30	0.20	0.29	0.254	0.28
Average of all directions		1.16	1 .23	1.41	1.01	1.05	1.12
Average of Southeast direction		1.59	1.64	2.01	1.33	1.39	1.49
Average of East		1.26	1.40	1.51	1.09	1.16	1.25
Average of West direction		0.83	0.78	0.93	0.78	0.77	0.82
X± S.D. of season		1.26±0.64			1.06±0.51		
t-value		-1.23					

Generally, from the obtained results we can observe that the maximum concentrations of soil Hg were recorded during February 2008 at all directions, but the highest concentrations were more pronounced in the dominant wind direction i.e., Southeast. A decline in Hg levels was obvious from March 2008 to June 2008 in all sampling directions. After March Hg levels started to increase again, but slightly from July to October 2008 as illustrated in Figure 5. Hg content in soil decreased with increasing distance from the hot spot in all directions.

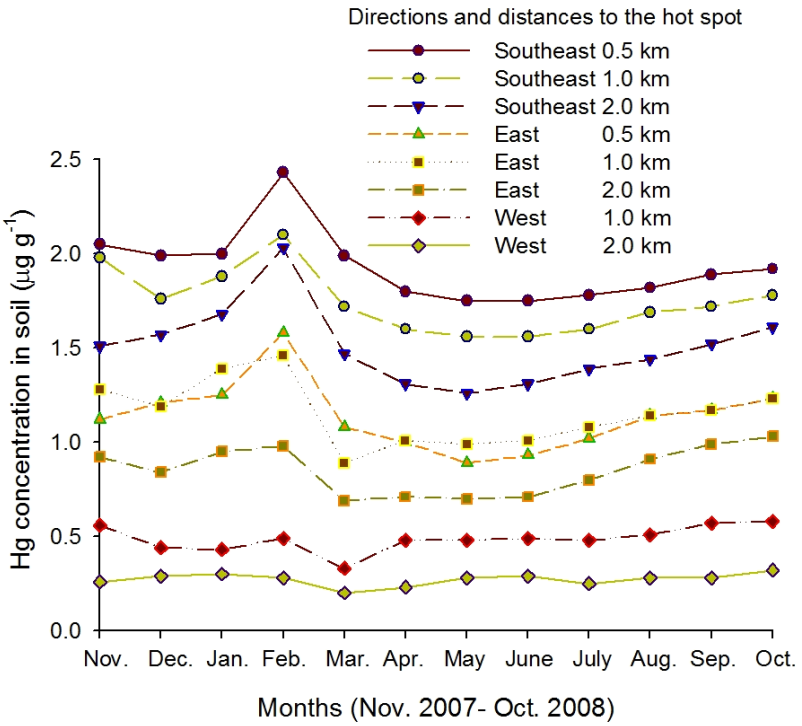

Figure 5. Distribution of Hg levels in soil with distances from the hot spot along with different sampling directions during the period of the study (Nov. 2007- Oct. 2008)

3.3 Mercury in plant

The plant samples were collected using the same procedure for air and soil samples. The levels of Hg in the unwashed plants in each site are presented in Table 5. The results showed variations of Hg levels in plant samples, these variations indicated that there is more than one factor affecting Hg uptake by vegetation. Mercury uptake can occurs by three major mechanisms i.e, (i) direct deposition from air on the plant, (ii) uptake from soil through roots , and (iii) uptake from air through the foliage in case of gaseous forms of Hg [25]. Temporal variations of Hg concentration in vegetation vary significantly (>10%) depending on tissue age and plant type [26]. In our study, the levels of total Hg in plant samples during the period of 12 months were relatively narrow compared with levels in air and soil which represented a great difference in the total Hg among different directions and sites. Concluding that plant Hg is not completely related to the surrounding environment as air Hg and soil Hg. The reason of this phenomenon can be attributed to the soil pH, where the Egyptian soils including Al-Max area have an alkaline nature. In this case most of Hg found in the precipitated form in the subsoil, therefore the absorption of Hg from the soil by plants is limited [27]. As a result, most of Hg in the studied plant samples were deposited from air and absorbed through plant leaves. Out of the above mentioned results it can be observed that, the limiting factor for plant pollution by Hg is the wind direction. Accordingly, air is the main source for plant pollution by Hg in Al-Max area depending on the wind speed and direction.

Table 5. Average, minimum and maximum concentrations of total Hg in plant samples (µg g^{-1}) in different directions at different distances from the hot spot. Plant samples collected from Al-Max area in Alexandria city during the study period (Nov. 2007 - Oct. 2008)

Variable	Southeast			East			West	
	0.5 km	1km	2 km	0.5 km	1 km	2 km	1km	2 km
Samples number/site	12	12	12	12	12	12	12	12
Average Conc. µg g^{-1}	1.97	1.73	1.55	1.23	1.33	0.97	0.98	0.79
Standard deviation	0.34	0.31	0.19	0.13	0.23	0.14	0.29	0.37
Minimum Conc. µg g^{-1}	1.5	1.33	1.34	1	0.94	0.79	0.38	0.34
Maximum Conc. µg g^{-1}	2.42	2.15	1.91	1.42	1.77	1.19	128	1.66

4. Conclusion

From the results obtained the following points can be concluded:

1. The limiting factors for environmental pollution by Hg in Al-Max area are wind speed, wind direction and distance to and from the pollution source.
2. The alkaline nature of the Egyptian soil including Al-Max area decreases the possibility for plant pollution with Hg. Where Hg is precipitated at the subsoil in different forms depending on the soil parent material and the occurrence of the soluble salts.
3. Plant pollution with Hg is not completely related to the surrounding environment as air Hg and soil Hg. In other words, only air is the main source for plant pollution with Hg and the soil has limited effect in this issue.

5. Recommendations

There are some recommendations are originated from our study:

1. The 2nd and the 3rd points of the conclusion initiates an idea for new study about the effect Hg on microbial activity in the soil and to what extent the soil microorganisms can utilize from Hg.
2. Continuous monitoring of Hg should be carried out in Wadi Al-Qamar area and especially after the change of mercury cells by membrane cells for the chlorine production in MCID as we have been informed during this study. Therefore, to recognize the expected change of Hg levels in this area another study is needed in the near future.
3. Continuous health monitoring for Wadi Al-Qamar residents should be carried out especially for children and pregnant women.
4. Enhancing the environmental awareness for both residents and workers through the governmental and non-governmental organizations.

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