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Evaluation of Soluble Non-Essential Trace Metals in Shatt Al-Hilla, Iraq

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In this study, the levels of non-essential trace elements, namely, aluminium, cadmium, lead and mercury, have been estimated in six different stations along Shatt Al-Hilla river in Babylon Governorate, Iraq. The findings provide baseline data on non-essential trace metal levels in Shatt Al-Hilla river water. The investigation has been monthly accomplished in six stations in Hilla city, Babylon Governorate, for the period between the 1st of November 2001 and the 31st of September 2002. The concentrations of the studied elements have been measured by using atomic absorption instrument type Shimadzu AA-670/gu-7 flame atomic absorption spectrophotometer and flameless graphite furnace. The concentrations of the elements, during the investigation period, were found to be in the ranges 434 ± 780, 114 ± 236, 36 ± 2 and 75 ± 39 μg L^{-1} respectively. Comparing these results with the WHO guidelines for the domestic waters revealed that the concentrations of the elements under investigation were within the elevated values. These findings demonstrate that waste materials have been got rid of into the Shatt Al-Hilla river, by human and/or industrial activities, leading to the contamination of the river. Also, a comparison with the previous studies on the river disclosed a decline in the Hg concentration. However, comparing this Hg concentration with that for other locations in Hilla city showed that the concentration falls within the high levels.

Key Words: Non-essential trace metals, Environment, Pollutant, Shatt Al-Hilla, River waters, Aluminium, Cadmium, Mercury, Lead.

INTRODUCTION

The accumulation of non-essential trace metals such as aluminium, cadmium, lead and mercury in aquatic environment has posed a potential risk to human health and the ecosystem. These elements are recognized to be toxic causing health implications without any beneficial effects to humans and wildlife[1, 2]. They

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are widely distributed in the environment. Their sources are essentially the weathering of soils and minerals[3, 4]. However, humans activities during the last decades have led to the increment of these metal levels[3, 5, 6]. Hence, the existence of these elements in the environment is regarded to be a source of enormous concern to the health practitioners, government establishments and the environmentalists.

Toxicity of non-essential metals takes place during the displacement of essential metals from their native binding sites or through ligand interactions. Moreover, at high levels both essential and non-essential metals can destroy cell membranes; modify enzyme specificity; disrupt cellular functions and damage the structure of DNA[7].

Aluminium existence in a natural water system poses a great potential threat to the health of a variety of species including humans[8, 9]. It takes part in calling forth dialysis encelopathy and dialysis osteodystrophy. In addition, it has a toxic effect upon the central nervous system[10, 11]. Some of the natural water sources such as rivers, lakes and domestic tap water contain aluminium in high concentrations *via* either the natural release of aluminium from sediments and soils through natural weathering as well as acidification routes or by the utilization of aluminium as flocculent throughout the purification process[12]. This demonstrates that aluminium ions have profound toxic effect on the individuals with renal dysfunction[11].

Cadmium, which is a non-essential element for living organisms[13], is well known to be one of the most toxic elements having carcinogenic effects upon the humans[14]. In addition, it has the capability to inhibit the ion exchange altering the permeability characteristics of the cell membranes. Moreover, it replaces zinc in specific enzymes leading to the disability of the functions of these enzymes as well as affecting of metabolism of glycogen, cholesterol and protein in the tissues of liver, kidney and the muscles of rats. Moreover, it accumulates mainly in the kidney and the liver, where high concentration gives rise to chronic kidney dysfunction. It causes a rapid infertility in animals. However, it is not certain whether they are human carcinogens, but cadmium replaces calcium in bones making them nonrigid[15]. Relating to the aquatic environment, cadmium causes coagulation of the external mucous layer in fishes leading to deficiency in the oxygen level in the tissues as well as changing the salt equilibrium and the incretion of the produced waste materials[16].

Lead is classified as being potentially hazardous and toxic to most forms of life[17]. It has proved to be responsible for quite a number of diseases in humans such as chronic neurological disorders especially in foetuses and children. Due to its easy contribution in the structures of enzymes especially with the thiol group, it is considered to be an enzymatic inhibitor. It inhibits the synthesis of haem and getting the avail from iron. In addition, it replaces calcium in bones as well as poisons the nerves and hence affects the brain. Besides, it produces slight alteration in the mental direction, dullness and weak memory. Moreover, it contradicts fertility beside having effects, which distort embryos in rodents[18, 19]. Automobile exhaust fumes are responsible for about 50% of the total inorganic lead absorbed by human beings[20]. Other sources of lead into the environment are from used dry-cell batteries, atmospheric deposition, sewage effluent and runoff of wastes.

Mercury and its compounds are very hazardous even in very low concentrations. Ingestion of aquatic organisms, particularly fish, is considered to be the main route for mercury to human beings. Mercury is the only metal which indubitably magnifies through the food chain. In addition, unlike most other metals, mercury is efficiently transformed into its most toxic form (methyl mercury) in the aquatic environment. This mercury methyl compound has high capability with the thiol (—SH) groups to inhibit the functions of some enzymes. Moreover, it can cause severe environmental and human health concerns, which depend upon the level and exposure duration. Short-term exposure to high levels of mercury gives rise to high blood pressure, damaging the lungs besides the common responses such as diarrhoea, nausea and vomiting. High level exposure is known to decrease neurotransmitter production, disrupt important processes within the nerve cells and decrease important hormones such as thyroid and testosterone. Besides, it can permanently damage the kidney and/or brain and may affect an unborn fetus. Children are highly affected *via* the impeding of their normal development. In the aquatic system, it may affect the appropriateness of fish species in terms of health and behaviour and in terms of the suitability of the fish for human consumption[20].

The increasing employment of these non-essential trace elements and their compounds in modern industries gives rise to the increment of their existence in surface water. Getting rid of the sewage as well as industrial materials, which are the major sources of the build up of these elements in the surface water, leads to the variation in water quality and ultimately hurts the living organisms. These risky substances which threaten the humans raised the necessity of investigating the non-essential trace elements in Shatt Al-Hilla river.

The object of the present study is to provide the baseline data on four non-essential trace metal levels, namely, cadmium, mercury and lead as well as the associated pH and total hardness values of water body in Shatt Al-Hilla river in Babylon governorate, Iraq. In addition, the project aimed, on the basis of these data, to determine the quality of this catchment, which is utilized for drinking, domestic, agriculture (*i.e.* irrigation and livestock watering) and aquatic ecosystem purposes.

EXPERIMENTAL

All chemicals used in this study were of analytical grade, supplied by BDH, of high purity ($\geq$ 99.9%) and were used as supplied.

Water samples were collected for the period between the 1st of November 2001 and the 28th of February 2002, by the same procedure as described before[21]. Fig. 1 shows the position of Shatt Al-Hilla on the world map.

A Shimadzu AA-670/GU-7 flame atomic absorption spectrophotometer and a flameless graphite furnace with deuterium background correction system were used successfully to reduce the background to an acceptable level. The instrument settings for the detection of the studied non-essential trace elements are cited below in Table-1.

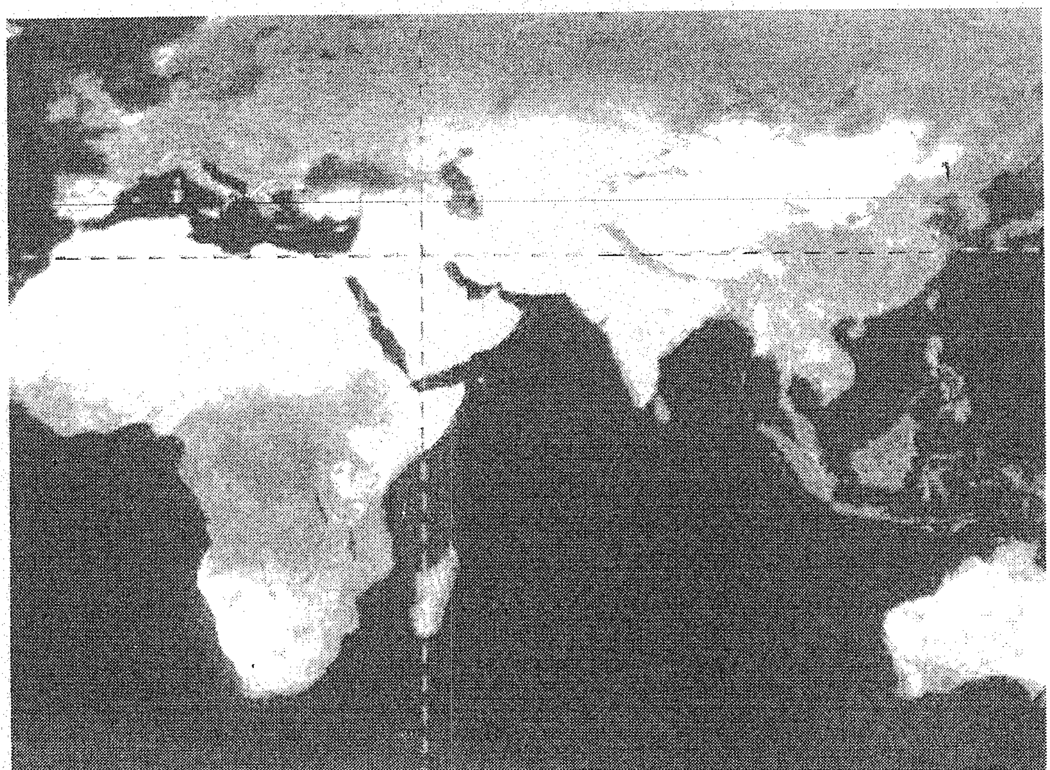

Fig. 1. Shatt Al-Hilla on world map

TABLE-1
INSTRUMENT SETTING FOR THE DETECTION OF THE STUDIED NON-ESSENTIAL TRACE METALS

Element	Mainline (nm)	Slit width (nm)	HCl current (mA)	Pyrolysis temp. (°C)	Atomization temp. (°C)
Al	309.3	0.8	6.0	1300	2400
Cd	228.8	0.8	3.0	900	1500
Pb	283.3	0.8	3.0	1200	2100
Hg	253.7	0.8	3.0	150	800

RESULTS AND DISCUSSION

The monthly alterations in temperature, pH and total hardness have been mentioned in our previous paper[21]. The concentration mean values of the dissolved non-essential trace elements under investigation, namely, aluminium, cadmium, mercury and lead in the water of Shatt Al-Hilla river, for all the six positions of the study, during all the periods of the study, were 434 ± 780, 114 ± 236, 36 ± 25 and 75 ± 39 $\mu g\ L^{-1}$ respectively.

Concerning aluminium, the mean value of 434 ± 780 $\mu g\ L^{-1}$ was higher than the WHO guideline for the domestic water of 200 $\mu g\ L^{-1}$.[22] In addition, the standard deviation value of 780, which is much greater than the mean value, indicated fluctuation in values. Actually, three high values far from the mean were of 4600, 1550, 5500 $\mu g\ L^{-1}$ for stations 1, 2 and 3 respectively, during February 2002. In addition, there were other three values of 1310, 1310 and 1400 $\mu g\ L^{-1}$ for station 6, during December, January and July 2002 respectively. These high levels for aluminium ascertain the pollution of the river waters as being due to the industrial and/or human activities.

Regarding the mean values for aluminium concentration in all of the stations with all the months, the levels ranged between 132 ± 204 and 948 ± 1642 $\mu g\ L^{-1}$. Also, the level mean values in all the stations per month diverged between 28 ± 8 and 2208 ± 2294 $\mu g\ L^{-1}$. Both ranges were higher than the above mentioned WHO guidelines for domestic employment of 200 $\mu g\ L^{-1}$, showing once again that the river waters were unsuitable for domestic use. Fatoki *et al.*[23] determined aluminium levels in the Umtata river, Eastern Cape, South Africa. The mean levels of aluminium in the river ranged between 220 and 360 $\mu g\ L^{-1}$ which were higher than the South African Target Water Quality Range (TQWR) of 0–150 $\mu g\ L^{-1}$in domestic water[24]. Moreover, the levels exceed the guidelines of 5 $\mu g\ L^{-1}$ for use of the aquatic ecosystem at pH 6.5 and 10 $\mu g\ L^{-1}$ at pH > 6.5.[24] Comparing the aluminium level in Shatt Al-Hilla river of 434 ± 780 with that obtained in the Umtata river of the range 220 to 360 $\mu g\ L^{-1}$ indicates that Shatt Al-Hilla river is highly polluted with aluminium.

Relating to cadmium, the mean value of 114 ± 236 $\mu g\ L^{-1}$ was obviously higher than the WHO guideline for the domestic water of 3 $\mu g\ L^{-1}$.[22] Also, the standard deviation value of 236, which is much greater than the mean value, indicates vacillation of the values. In fact, three high values were found to be far from the mean, namely, 590, 1145 and 1370 for stations 4, 5 and 6 respectively, during August 2002. These elevated levels for cadmium establish the pollution of the river waters with this metal as being due to the industrial and/or human activities.

Concerning the mean values for cadmium in all the stations with all the months, the values were changed from 27 ± 18 to 196 ± 410 $\mu g\ L^{-1}$. Moreover, the mean values in all the stations per month were of the range 13 ± 2 to 552 ± 587 $\mu g\ L^{-1}$. In fact, both the ranges were higher than the above mentioned WHO guidelines of 3 $\mu g\ L^{-1}$, demonstrating once again that the river waters were inappropriate for domestic employment. In the investigation mentioned above carried out by Fatoki *et al.*[23] on the trace metals in the Umtata river, the concentration mean of cadmium was found to vary between 10 to 260 $\mu g\ L^{-1}$ which reveals that the levels were higher than the tentative South African guidelines of 0–5 $\mu g\ L^{-1}$ in water used domestically.[24] These results prove that cadmium levels of 114 ± 236 $\mu g\ L^{-1}$ in Shatt Al-Hilla river were greatly higher than those observed in Umtata river.

Concerning lead, the mean value of 75 ± 39 $\mu g\ L^{-1}$ was much higher than the WHO guideline for the domestic water of 10 $\mu g\ L^{-1}$.[22] In addition, the standard deviation value of 39, which is high, indicated fluctuation of the values. Actually, one high value far from the mean was of 123 $\mu g\ L^{-1}$ for station 1 during January 2002. Moreover, another four high values of 100, 110, 100.125 and 110 $\mu g\ L^{-1}$, for stations 1, 2, 3, 5 and 6 respectively, were recorded during March 2002. These high levels for lead point out the pollution of the river waters as being attributable to the industrial and/or human activities.

Regarding the lead concentration mean in all the stations through all the months, the values ranged between 71 ± 39 and 83 ± 47 μg L^{-1}. These values, on the other hand, the mean value range of all the stations per month varied from 53 ± 14 to 105 ± 14 μg L^{-1}. Both the ranges are much greater than than the WHO guideline of 10 μg L^{-1}.[22] Undoubtedly, both the ranges reveal the inappropriateness of river waters for domestic utilization. In a study carried out by Awofolu *et al.*[25] on the Tyume River water, Eastern Cape Province, South Africa, the results showed that the concentrations of lead ranged between 21 ± 4 and 35 ± 1 μg L^{-1}. This range was greater than that of TWQR of 0–10 μg L^{-1} in river water for domestic use. These high levels of lead were ascribed to the sediment as an influential factor besides other enhancing parameters such as the current flow and pH since water acidity is well known to affect the solubility and availability of metals. Comparing the lead levels in Tyume River water with that noticed in Shatt Al-Hilla river of 75 ± 39 μg L^{-1} obviously reveals the higher levels in the latter river compared with the former one.

Pertaining to mercury, the mean value of 36 ± 25 μg L^{-1} was awfully higher than the WHO guideline for the domestic water of 1 μg L^{-1}.[22] In addition, the standard deviation value of 25, which is considered to be high, reveals the fluctuation of the values. Actually, four high values far from the mean were of 80, 90, 75 and 70 μg L^{-1} for the stations 2, 3, 5 and 6 respectively, during November 2001. In addition, another four values were 80, 85, 75 and 65 μg L^{-1} for stations 2, 3, 5 and 6 respectively, during December 2001. Moreover, another concentration of 70 μg L^{-1} was noticed for station 6 through February 2002. These high levels for Hg demonstrate that Shatt Al-Hilla river is highly polluted with mercury. Industrial and/or human activities were responsible for this pollution.

Regarding the mean values for mercury in all the stations with all the months, the values ranged between 30 ± 17 and 40 ± 29 μg L^{-1}. On the other hand, the mean value range of all the stations per month was from 13 ± 4 to 69 ± 18 μg L^{-1}. Indeed, both the ranges are much greater than the WHO guideline of 1 μg L^{-1}.[22], revealing that the river waters were unsuitable for domestic utilization. In their study on the trace metals in four rivers of the Eastern Cape Province, South Africa, namely, Buffalo, Keiskamma, Thyume and Umtata rivers, Fatoki and Awolfolu[26] reported the levels of the trace metal mercury to range from trace to 3 ± 1, trace, trace and trace to 3 ± 1 μg L^{-1} respectively. The South African guideline for mercury in water for domestic, ecosystem and aquaculture uses is 1 μg[24, 12, 20]. On the basis of this guide, the levels of mercury are considered generally low in the rivers. Comparing these levels with those obtained in Shatt Al-Hilla river of 36 ± 25 μg L^{-1} shows that mercury levels in the latter are considerably high on the basis of South Africa guideline.

In summary, the mentioned detected levels for the non-essential trace metals under investigation, namely, aluminium, cadmium, lead and mercury are higher than the WHO guidelines for these metals, which are 200, 3, 10 and 5 μg L^{-1} respectively[22].

Different environmental parameters, which operate synchronously, lead to the chemical composition of water, but with different effects and efficiencies. Our previous paper[21] investigated the effects of temperature, pH, total hardness. In addition, it comprises the estimation of the essential trace metal including chromium, cobalt, copper, iron, manganese, molybdenum, nickel, selenium, vanadium and zinc[21]. These results assure the highness of the detected levels. As mentioned before, the river is widely employed in three governorates for domestic, irrigation of agricultural territories and industrial purposes. In addition, it is a source of many commercial fish used as food by humans.

In view of this wide usage of this catchment, the high levels of elements are of great concern. For instance, cadmium is of extreme apprehension because of its high toxicity to humans. In addition, using the river in feeding livestock imposes a guideline of 10 $\mu g\ L^{-1}$ which was also exceeded and hence may lead to chronic cadmium metal poisoning in the livestock. To be used by the ecosystem, cadmium concentration is of 15 $\mu g\ L^{-1}$ in soft water and 25 $\mu g\ L^{-1}$ in moderately soft water[12]. These guidelines were surpassed rendering the river not suitable for aquatic ecosystem.

Regarding mercury and on the basis of the mentioned guidelines, the element poses a problem to water with the above stated uses. Also, lead exceeded the acceptable level which means that using the water by man and animals may give rise to accumulation of the metal resulting in ill-health consequences, such as growth retardation in children[27].

The results were statistically analyzed, using Completely Randomized Design (CRD), to accomplish a comparison among the stations with respect to all the studied parameters. The Least Significant Difference (LSD) has been found with a probability of 0.01 and 0.05. In addition, the *t*-test was employed for a comparison among the different months of the year for each of the investigated parameters. No significant difference among the stations was seen with all the studied parameters.

Concerning the comparison among the months, significant differences were noticed in all the stations with a probability level of 0.05 for all the parameters except aluminium and the pH for station 1 and mercury, lead and pH for station 3.

Additionally, the correlation coefficient (R), among all the studied parameters, was calculated. The results have shown the existence of a direct significant relation between cadmium and the water temperature. On the other hand, inverse relation was revealed for mercury with chromium, cadmium, water temperature and pH. The water temperature was found to correlate directly with pH. Finally, pH has a direct relation with total hardness.

Concerning the significant differences, aluminium revealed no significant differences in its concentration among the the six stations. However, due to the variation of the months, significant differences in the stations 2, 3, 4, 5 and 6 with a probability level of 5.1% were observed, whereas station 1 did not demonstrate any significant differences. Also, cadmium showed no significant differences in the concentration of the element among the the six stations. However, all the stations revealed significant differences during the months with a probability level of 5.1%.

In addition, mercury demonstrated no significant differences in the concentration of the element among the six stations. Nevertheless, stations 1, 2, 4, 5 and 6 revealed significant differences with a probability level of 5.1% with the variation of months. No significant difference was noticed with station 3.

Finally, lead disclosed no significant differences in the concentration of the element among the six stations. However, stations 1, 4, 5, 6 demonstrated significant differences with a probability level of 5.1%, during the months. Nevertheless, with station 2 significant difference was revealed with a probability level of only 5.0%, whereas with station 3 no noticeable significant difference was detected throughout the months.

Regarding the factors affecting the concentration of the studied trace metals, the water temperature showed no significant differences in the concentration of the element among the six stations. However, all the stations showed significant differences with a probability level of 5.1% through the variation of the months.

Besides, the total hardness parameter demonstrated no significant differences in the concentration of the element among the six stations. On the other hand, the variation of the months gave rise to significant differences with a probability level of 5.1% in all the stations.

Lastly, the pH revealed no significant difference in the concentration of the element among the six stations. Nevertheless, with the variation of the months, station 6 demostrated significant differences with a probability level of 5.1%, whereas stations 4 and 5 led to significant differences with a probability level of only 5.0%. Yet, no significant differences have been obtained in the stations 1, 2 and 3. Table-2 demonstrates the correlation of the measurements.

TABLE-2
THE CORRELATIONS OF THE MEASUREMENTS

Elements	Relation type	R-value	Probability level
1. Aluminium			
Zinc	Direct	0.33	0.05
2. Cadmium			
Mercury	Inverse	0.33	0.05
Iron	Inverse	0.50	0.01
Chromium	Inverse	0.40	0.05
Vanadium	Direct	0.67	0.01
Temperature of water	Direct	0.49	0.01
Total hardness	Direct	0.38	0.05
3. Lead			
Iron	Direct	0.50	0.01
Manganese	Direct	0.42	0.01
Nickel	Direct	0.50	0.01

Elements	Relation type	R-value	Probability level
4. Mercury			
Cadmium	Inverse	0.33	0.05
Cobalt	Inverse	0.59	0.01
Chromium	Direct	0.33	0.05
Manganese	Inverse	0.53	0.01
Nickel	Inverse	0.48	0.01
Vanadium	Inverse	0.77	0.01
Zinc	Direct	0.64	0.01
Teperature of water	Inverse	0.64	0.01
pH	Inverse	0.39	0.05

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