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Essential Trace Metals Concentrations in River Waters in Hilla Governorate, Central Iraq

FALAH H. HUSSEIN*, MAYSON M. AL-TAEE, AHMED N. ALKHATEEB† and FADHIL M. ABID‡

Chemistry Department, College of Science for Women
University of Babylon, Babylon Governorate, Iraq
E-mail: abohasan_hilla@yahoo.com

The purpose of this work was to provide information on essential trace metals concentrations in Shatt Al-Hilla in Babylon governorate, Iraq. Six sampling stations were chosen along Shatt Al-Hilla, which is a branch of Euphrates river. Water samples were analyzed for temperature, pH and total hardness. The concentrations of the essential trace metals such as chromium, cobalt, copper, iron, manganese, molybdenum, nickel, selenium, vanadium and zinc were evaluated. Water samples from six stations were collected during the period between the 1st of November 2001 and 31st of September 2002. The concentrations of the elements, during the study period, were found to be 40 ± 23, 46 ± 29, 77 ± 43, 60 ± 33, 36 ± 21, 283 ± 217, 50 ± 27, 35 ± 20, 1314 ± 950 and 70 ± 84 $\mu g\ L^{-1}$ respectively. Comparing these results with those recorded for some other rivers as well as the WHO domestic water guidelines, demonstrated that the concentrations of the elements fall within the high values, indicating that waste materials have been thrown into the river which became polluted. However, concentrations of cobalt, iron and manganese were within the WHO limits.

Key Words: Essential trace metals, Environment, Pollutant, Shatt Al-Hilla, River waters, Chromium, Cobalt, Copper, Iron, Manganese, Molybdenum, Nickel, Selenium, Vanadium, Zinc.

INTRODUCTION

The term trace metals is generally given to the elements found in little concentrations in the natural bio-system[1]. The aquatic environment contains trace elements in different forms, including the dissolved and the particulate trace metals. The ions, which are either free or connected to organic or inorganic compounds or colloidal molecules, have the ability to pass across the filters of the type 0.45 μm millipore membrane. The particulate trace metals, which have molecules of diameters > 0.45 μm, comprise two types of particles. The first one is biological and includes microorganisms, such as the botanical and zoological ramblers, bacteria, fungi and the metabolic products. The second type of particulates is non-biological and embraces the inorganic as well as the organic chemical compounds like mud, alluvia, feldspar, quartz and the calcite and silica compounds, organic crumbs as well as the compounds resulting from the combination of the dissolved and the colloidal molecules with each other beside organic compounds such as the humus acids and the amino acids[2, 3].

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†Chemistry Department, College of Science, Ibb University, Ibb, Yemen.
‡Chemistry Research Center, Ministry of Science and Technology, Iraq.

The trace elements are divided, according to their importance to the human body, into two groups. The non-essential trace elements which include the elements silver, aluminium, cadmium, gold, lead and mercury[4], which have no biological role, are non-essential and potentially toxic to living organisms, specially microorganisms. The second group is called the essential trace elements which embraces calcium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, nickel and zinc. These elements play an integral role in the life processes of living organisms. They are serving as micronutrients and are utilized for redox-processes, to stabilize molecules *via* electrostatic interactions, as components of various enzymes and regulation of osmotic pressure. Toxicity of nonessential 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 nonessential metals can destroy cell membranes, modify enzyme specificity, disrupt cellular functions and damage the structure of DNA.

Concerning the essential trace elements, some of them are involved in bio-structures like the metalloenzymes whereas others activate many enzymes such as arginine desimidase, aminopolypeptidase and phosphomonesterase, which are important for the human being due to their involvement in the composition of vitamin B_{12}.[5–7]

Chromium(III) was demonstrated to be important in monitoring the metabolic process for fats and glucose *via* the activation of the phosphoglucomutase[5–7].

Cobalt achieved its essentiality from its involvement in some metabolic activities in organisms. Nonetheless, large amounts of the element have toxicological outcomes including flushing, vasodilation and cardiomyopathy in humans and animals[8].

Copper has a special importance as a respiratory pigment, which transfers the electrons within the cytochrome system[9].

Iron and manganese are essential in the activation of the functions of the living organisms. In addition, both are engaged in the structure and activation of a number of oxidizing enzymes. Iron has a special importance in the life of the human beings as well as the living organisms in the botanical and zoological kingdoms, where it functions as a respiratory pigment in addition to its engagement in the structure of the catalase enzyme[10]. Manganese plays an important role in the building of connective tissues and bony tissues[7].

Molybdenum is considered to be essential for the human being as well as the animal, where it is bound in three types of metallic enzymes, namely, xanthine oxidase, aldehyde oxidase and sulfate oxidase. The first enzyme is involved in the decomposition of purines into boric acid, whereas the second one activates the oxidation of aldehydes. The last enzyme stimulates the oxidation of amino acids containing sulfur during the final stages[7].

Nickel takes part in the ordinary metabolism in micro-organisms that fix the nitrogen by affecting the hydrogenase enzyme[11]. A number of studies have pointed out that nickel has a nutrient importance, where it is engaged in the composition of the nucleic acids, DNA and RNA. However, nickel-related health effects such as cardiovascular and renal effects in animals have been reported[12]. Nickel's toxic effects upon humans are related to dermal, lung and nasal sinus cancers.

Selenium is well known to be of fundamental importance for human health. As a constituent of selenoproteins, selenium has structural and enzymic roles, in the latter context being best known as an antioxidant and catalyst for the production of active thyroid hormone. Selenium is required for the appropriate functioning of the immune system and represents the key nutrient in counteracting the development of virulence and inhibiting HIV progression to AIDS. It is required for sperm motility and may lessen the danger of miscarriage. Shortage of the metal has been associated with adverse mood states. An elevated selenium intake could be combined with reduced cancer risk[13].

Regarding vanadium, the element has a role in the thyroid metabolism. In addition, its compounds have anti-tumour activity[7].

Concerning zinc, it is an essential element in the conservation of the structure and functions of the cell membrane[11]. In addition, it has a very big role in the growth of plants and animals, where it is considered to be one of the important components for about 300 enzymes in plants as well as a number of enzymes in the humans such as RNA and DNA polymerase, alkaline phosphatase and carbonic anhydrase[7]. However, despite the fact that zinc has low toxic effect to humans, prolonged consumption of large amounts may give rise to some health complications like dizziness, fatigue and neutropenia. In addition, some reports demonstrated that zinc could be toxic to some aquatic organisms like fish[14].

The ascending usage of these trace elements and their compounds in modern industry has brought about an increment of their existence in surface water. Throwing down of the industrial and sewage waste substances, which are the main sources of the accumulation of these elements in the surface water, gives rise to the alteration of the water quality and ultimately the injury to the living organisms. These hazards which threaten human life have emphasized upon the necessity of studying trace elements in Shatt Al-Hilla.

The objectives of this study were firstly to estimate the distribution of the dissolved essential heavy metals such as chromium, cobalt, copper, iron, manganese, molybdenum, nickel, selenium, vanadium and zinc in Shatt Al-Hilla in Hilla Governorate, Iraq and the associated pH and total hardness values of water bodies. Secondly, on the basis of these data the quality of this catchment, which is used for drinking, domestic, agriculture (*i.e.* irrigation and livestock watering) and aquatic ecosystem purposes, could be determined.

EXPERIMENTAL

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

The river water samples have been collected, periodically (monthly) for the period which started from the 1st of November 2001 up to the 28th of February 2002, from the underwater to avoid any possible pollution, using polyethylene containers, which were re-cleaned in the laboratory by an acid. These samples were filtered by using filters of the type 0.45 μm millibore membrane. The element concentrations were determined by utilization of the atomic absorption instrument of the type Sdzu AA-670/Gu-7 flame atomic absorption spectrophotometry and flameless graphite furnace.

The locations of the six chosen stations, along Shatt Al-Hilla river, are shown in Fig. 1. The sampling stations were chosen to reflect different activities. Station 1 is outside Hilla city, *i.e.*, before the entrance of the river to the centre of Al-Hilla city.

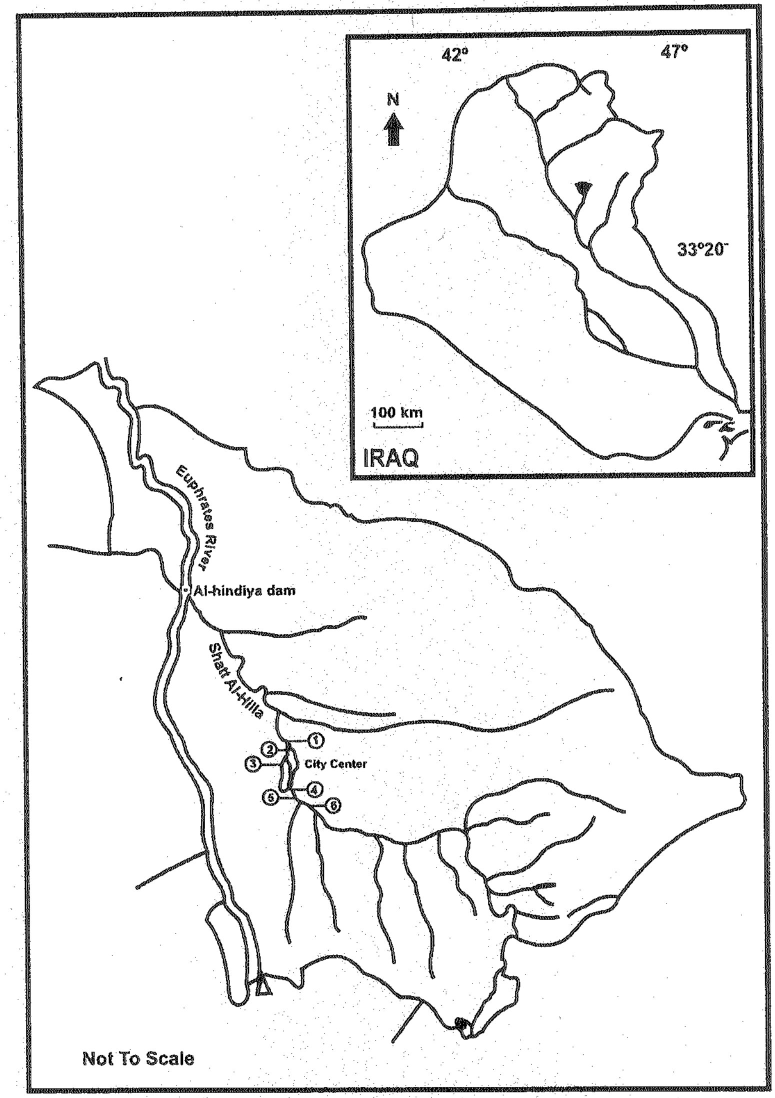

Fig. 1. Sampling positions

Station 2 is situated after the entrance of the river to the city centre. Station 3 represents the city centre, whereas station 4 is positioned after the lay down position of the waste materials thrown by the Al-Hilla textile manufactory. Station 5 is situated after the position of the sewage drainage from Al-Hilla sewage station in Almeaimira, whereas Station 6 is positioned after the water pump station, which is located between Al-Saada and Al-Nekhiala villages.

Description of study area: Shatt Al-Hilla has been chosen as a study location because of the significance of this river as being widely employed for irrigating the agricultural territories in three governorates. Besides, it is utilized for domestic and industrial purposes. Moreover, it is regarded as a source of many commercial fish used as food by humans.

Since Shatt Al-Hilla is a branch of the Euphrates river, it is necessary to disclose some information about Euphrates. The Euphrates river flows out north of Erzerum in Turkey, where the highest mountain surpasses 3000 m above sea level. The sources are situated between the Black Sea and Lake Van and the river is formed by the confluence of two tributaries, the Murad-Sue, which emerges from many springs in the area of Ala-Dag and flows from the south and the Kara-Sue, which begins in the Kargapazari Mountains, north of Erzerum and flows from the north to meet at a point near the village of Keban. The Murad-Sue river is 650 km long and the Kara-Sue river is 450 km long. These tributaries contribute 75 per cent of the Euphrates water. From 1,000 m above sea level in north Anatolia, the river is then known as the Euphrates[15, 16].

10 km downstream from the confluence, there is a narrow gap where the Keban Dam has been constructed. The most important tributary is the Tokhma Sue which drains the Taurus mountains and joins the Euphrates close to the town of Malorteya. Beneath the village of Keban, the Euphrates flows down the sharp slopes on the southern border of the mountains of the Kurdestan and Armenian areas and enters the region of the eastern plains of Syria. The total length of the Euphrates in Turkey is 455 km, from the point of confluence of the Kara-Sue and Murad-Sue until it enters Syria at the town of Trablus.

Having crossed the Iraqi border, the Euphrates continues its flow in a south-easterly direction, crossing the desert highlands and narrow valleys which terminates at Ramadi before entering the Mesopotamian plains. Though the Euphrates comes very close to the Tigris near the town of Falluja, it once again moves away from it in the southern direction.

Downstream from the town of Mussaiyab and upstream of the Hindiya barrage many large canals withdraw water from the Euphrates river. The most important is Shatt Al-Hilla (called Shatt Al-Hindiya at this point), which passes the Hindiya barrage and then flows through the towns of Hindiya and Kifil (Fig. 1).

Downstream from Kifil it splits into two branches: the Kufa-112 branch on the west and the Shamiya branch on the east. The Kufa branch is again divided downstream from the town of Abu Shukhir into the Jehad and Mishkhab branches while the Jehad branch terminates in an area of agricultural land where its waters are completely utilized for irrigation purposes. The Mishkhab branch (of the Kufa branch) continues to flow in a southern direction and goes across Mishkhab, Qadisiya and then to the south of Shinafiya. Here the river runs into many branches which join each other to the north of the town of Nasiriya. From Nasiriya the river again streams into many branches towards the town of Souk-al-Shiukh and all these branches discharge into the Hammar Marshes. From the Hammar Marshes the Euphrates waters flow into Shatt Al-Arab, near Karmat-Ali.

The total length of the Euphrates from the confluence of the Kara-Sue and Murad-Sue to its confluence with Shatt-al-Arab near Karmat-Ali is about 2330 km, whereas its total length approaches 1200 km[15–16].

Shatt Al-Hilla is a left branch of Euphrates in the forehead of Al-Hindiya dam, with a current length of 160 km. Its pathway includes two ankhs: the first one is of 3 km length, whereas the second one is of 5 km. The discharge of Shatt Al-Hilla in its forehead is 250 m^3 sec^{-1}. This discharge is variable depending upon the requirements of agriculture in the three governorates irrigated by it, namely, Babylon, Al-Qadisiya and Al-Mothanna governorates with a total area of 420,000 ha[17]. The maximum level for Shatt Al-Hilla in the forehead area is 31.6 m, while it is 28.9 m inside Hilla city. Its slope is of 7 cm km^{-1}.

The sedimentations inside Shatt Al-Hilla depend on different factors, such as source of waters, sector of Shatt Al-Hilla, speed of waters and straightening of the river.

Euphrates is supplied with water from abroad as well as the income from Al-Thirthar trough, Al-Habbaniya lake and the lake Al-Qadisiya dam in Hadeetha. This, in turn, affects the composition as well as the quality of Shatt Al-Hilla water, where the water coming from abroad carries the alluvial and the other suspensions curetted by rainwaters, whereas the waters of the lakes such as Al-Habbaniya and Al-Thirthar bear the sand, algae, seeds and the other botanical suspensions.

RESULTS AND DISCUSSION

Shatt Al-Hilla river has been chosen as a study location due to the importance of this water source which is widely used for agricultural purposes, where it irrigates the agricultural lands in three governorates. In addition, it is employed for domestic, drinking and industrial purposes. Moreover, it is considered to be a source of many commercial fish which are used as food by human beings.

Tables 1–3 reveal the monthly alteration of temperature, pH, total hardness in the water of Shatt Al-Hilla, for the different locations of this study.

Regarding the temperature, the alteration of the mean values of all of the stations with months varied between 20.94 ± 11.57 and 21.5 ± 11.86°C, which were higher than the Canadian Drinking Water Quality Guideline (CDWQ) of 15°C[18]. In addition, Table-2 shows that the variation of temperature with months is due to the alteration of seaons. For instance, in all the stations, the high temperatures were observed in July and August. The variation of the temperature mean values through the stations with each month ranged between 12.25 ± 0.41 and 30.16 ± 0.41, which demonstrated once again the highness of the temperatures compared with the CDWQ guideline of 15°C[18]. However, the results obtained in Table-1 reveal that the temperatures for all the stations within the same month were nearly the same, indicating that the temperature is independent of the stations under investigation.

Pertaining to the pH, Table-3 illustrates that the alteration of the mean values of all the stations with months varied between 7.40 ± 3.59 and 7.79 ± 3.66°C, indicating that these levels were within the WHO guideline of 6.5–8.5[19]. The variation of the pH mean values *via* the stations with each month varied from 6.6 ± 0.64 to 8.08 ± 0.16, demonstrating that the levels follow the mentioned WHO guideline[19].

TABLE-1
ALTERATION OF TEMPERATURE

Station	Sampling dates								
	11/2001	12/2001	1/2002	2/2002	3/2002	7/2002	8/2002	9/2002	Mean
1.	23.3	14.4	15.5	11.5	16.5	30	30.0	27.5	21.088 ± 11.679
2.	23.5	14.5	14.0	12.0	17.0	30	29.0	27.5	20.938 ± 11.568
3.	23.6	17.6	14.0	12.0	17.0	30	30.0	27.0	21.400 ± 11.663
4.	23.4	14.7	14.5	12.5	17.5	30	30.5	27.5	21.325 ± 11.735
5.	23.5	14.9	14.5	12.5	17.5	30	30.0	27.5	21.300 ± 11.677
6.	24.1	14.9	14.5	12.5	17.5	31	30.5	27.0	21.500 ± 11.859
Mean	12.56 ± 0.28	15.2 ± 1.21	14.5 ± 0.55	2.25 ± 0.41	17.25 ± 0.41	30.16 ± 0.41	30.00 ± 0.55	27.25 ± 0.26	–

TABLE-2
pH

Station	Sampling dates								
	11/2001	12/2001	1/2002	2/2002	3/2002	7/2002	8/2002	9/2002	Mean
1.	7.5	7.9	7.0	6.0	8.1	7.9	8.4	8.0	7.59 ± 3.61
2.	7.5	8.0	7.0	7.5	8.2	8.3	7.9	7.9	7.79 ± 3.66
3.	7.3	8.0	6.7	7.3	8.0	8.1	7.9	7.5	7.57 ± 3.57
4.	7.6	8.1	6.7	6.4	8.0	8.1	8.0	7.9	7.60 ± 3.59
5.	7.8	8.1	5.7	6.0	8.1	8.2	8.0	7.9	7.40 ± 3.59
6.	8.0	8.2	6.7	6.6	8.1	7.9	8.0	8.0	7.69 ± 3.63
Mean	7.6 ± 0.25	8.05 ± 0.11	6.7 ± 0.48	6.6 ± 0.64	8.08 ± 0.08	8.08 ± 0.16	8.03 ± 0.19	7.87 ± 0.19	–

TABLE-3
TOTAL HARDNESS

Station	Sampling dates								
	1/2001	12/2001	1/2002	2/2002	3/2002	7/2002	8/2002	9/2002	Mean
1.	230	520	700	520	250	892.8	961.0	954.8	628.58 +. 384.66
2.	230	540	780	460	260	930.0	892.8	998.2	636.38 ± 391.70
3.	250	530	540	440	240	899.0	954.8	899.0	594.10 ± 368.88
4.	280	600	760	450	310	930.0	936.2	1054.0	665.03 ± 399.22
5.	290	620	840	620	350	868.0	923.2	954.8	683.25 ± 385.00
6.	240	650	680	620	330	942.4	905.0	998.0	683.18 ± 384.89
Mean	270.00 ± 42.43	576.67 ± 42.43	716.66 ± 53.92	518.33 ± 83.53	256.66 ± 46.04	927.03 ± 28.39	928.83 ± 24.70	976.47 ± 52.70	–

Concerning the total hardness, Table-4 revealed the variation of the mean values of all the stations with all the months to be ranged from 594.1 ± 368.88 to 683.18 ± 385.00 mg L^{-1}. This range is lower than the guideline of the WHO of 1000 mg L^{-1}.[19] Moreover, the mean value change through all the stations for each month varied between 256.66 ± 46.04 and 976.47 ± 52.70, pointing out that the river waters in all the stations were suitable for domestic use with regard to total hardness.

Regarding the dissolvable essential trace metals, the concentration mean values for the elements chromium, cobalt, copper, iron, manganese, molybdenum, nickel, selenium, vanadium and zinc have been found to be 40 ± 23, 46 ± 29, 77 ± 43, 60 ± 33, 36 ± 21, 283 ± 217, 50 ± 27, 35 ± 20, 1314 ± 950 and 70 ± 84 $\mu g\ L^{-1}$ respectively.

With regard to chromium, the stated mean value of 40 ± 23 $\mu g\ L^{-1}$ was lower than the WHO guideline for domestic water of 50 $\mu g\ L^{-1}$.[19] However, the high standard deviation value of 23 $\mu g\ L^{-1}$ indicated some fluctuation of the values. In fact, two high values of 65 and 60 $\mu g\ L^{-1}$, which were far from the mean, have been recorded during November 2001, for the stations 1 and 5 respectively. In addition, a value of 54 $\mu g\ L^{-1}$ was observed for station 2 during December 2001.

On the other hand, two high values of 63 and 90 μg L^{-1} were noticed for stations 1 and 2 respectively, during January 2002. Moreover, stations 1 and 2 revealed two values of 70 and 55 μg L^{-1} respectively in February 2002. Finally, six high values of 86, 66, 70, 69, 55 and 61 μg L^{-1} were demonstrated for the stations 1, 2, 3, 4, 5 and 6 respectively, for September 2002. These high levels for chromium ascertain the pollution of the river waters during the stated periods, as being due to the industrial and/or human activities. Concerning the mean values for chromium concentrations in all of the stations with all the months, the levels ranged between 33 ± 20 and 51 ± 30, which were within the mentioned WHO guideline of 50 μg L^{-1},[19] as well as the South African Target Water Quality Range (TQWR) of 50 μg L^{-1} for domestic water[20]. Additionally, the level mean values in all the stations per month diverged between 16 ± 2 and 68 ± 11 μg L^{-1}. Both the ranges of chromium levels show that the river waters, with regard to chromium, could be considered suitable for domestic use. An investigation has been carried out by Gulfraz *et al.*[21] to detect, among several trace metals, the concentrations of chromium in Rawal and Mangla lakes, Pakistan. The study was established between January and December 1997. The level mean value of chromium was obtained to be 117 ± 12 μg L^{-1}, which is much greater than the WHO permissible limit of 50 μg L^{-1}.[19] These high concentrations were regarded as originating from municipal wastewater and geological weathering. In comparison with chromium value of 40 ± 23 μg L^{-1} in Shatt Al-Hilla river, Cr in the latter is much lower than that in the former.

Relating to cobalt, the mentioned mean value of 46 ± 29 μg L^{-1} was lower than the South African Target Water Quality Range (TQWR) for domestic water of ≤ 2000 μg L^{-1}.[22] This ascertains, with regard to Co, the suitability of Shatt Al-Hilla river waters for domestic use. However, the elevated standard deviation value of 29 μg L^{-1} indicates the fluctuation of some values. Actually, one high value far from the three values of 55, 55 and 55 μg L^{-1} for stations 1, 2 and 6 respectively, was the recorded mean was of 60 μg L^{-1} for station 2 during November 2001. In addition, another three values of 55, 55 and 55 μg L^{-1} for stations 1, 2 and 6 respectively, were recorded during January 2002. A value of 54 μg L^{-1} for station 3, in February 2002, was also noticed. Besides, three values of 78, 70 and 64 μg L^{-1} were obtained for stations 1, 2 and 6 in March 2002. Other obtained values were of 90, 70 and 70 for the stations 3, 5 and 6 respectively, during April 2002. One value of 54 μg L^{-1} was detected for station 5, in July 2002. Finally, three high value of 132, 64 and 56 μg L^{-1} were obtained for the stations 1, 2 and 3 respectively, during August 2002. The above mentioned high values for the indicated months demonstrate an obvious indication of man-induced and/or industrial pollution, during the cited periods.

Regarding the mean values for cobalt concentration in all of the stations for all the months, the levels ranged between 30 ± 21 and 61 ± 39 μg L^{-1} which were lower than the South African Target Water Quality Range (TQWR) for the domestic water of ≤ 2000 μg L^{-1}.[20] Besides, the levels of cobalt mean values in all the stations per month diverged between 16 ± 14 and 60 ± 1354 μg L^{-1}. Both ranges of cobalt levels show that the river waters, with regard to Co, were suitable for domestic use[20]. In a study conducted by Awofolu *et al.*[22], to detect the levels of cadmium, lead, cobalt, zinc, copper and nickel in the Tyume river water, Eastern Cape, South Africa, the results showed that the concentrations of cobalt fell in the range 0–62 ± 2 µg L^{-1}, which were higher than the typical concentration of the element of 0.2 µg L^{-1} in unpolluted surface water. However, adverse chronic effects of cobalt ingestion at concentration > 2000 µg L^{-1} may occur[20]. On the other hand, the water was considered to be quite suitable for agricultural employment and livestock watering, where no adverse effect was noted even at TWQR of 0–1000 µg L^{-1}. Contamination with cobalt has been attributed, in part, to the wastes of some metal alloys and cobalt salts in some pigments. Comparing the cobalt levels in Shatt Al-Hilla river of 46 ± 26 µg L^{-1} with that recorded in the Umtata river of the range 0–62 ± 2 indicates that Shatt Al-Hilla river is less polluted with cobalt. However, there is some instability in the values of cobalt in Shatt Al-Hilla river with variation of the stations and months as well.

With regards to copper, the stated mean value of 77 ± 43 µg L^{-1} was lower than the WHO guideline for domestic water of 1000 µg L^{-1}.[19] This reveals, as regards copper, the appropriateness of Shatt Al-Hilla river waters for domestic use. However, the high standard deviation value of 43 µg L^{-1} indicate vacillation of some values. Actually, five high values of 94, 140, 160, 140 and 115 µg L^{-1} were recorded for stations 1, 2, 3, 5 and 6 respectively, during December 2001. Besides, two high values of 85.90 µg L^{-1} for stations 1 and 3, respectively, were noticed during January 2002. In addition, two values of 90 and 100 µg L^{-1} were recorded for the stations 2 and 3 respectively, throughout March 2002. Furthermore, one value for station 1 during April 2002 was recorded. Moreover, five values of 97, 98, 100, 103 and 103 µg L^{-1}, for stations 1, 2, 3, 5 and 6 respectively, were noticed during July 2002. Finally, two values of 125 and 140 µg L^{-1}, for stations 2 and 5 respectively, were observed during August 2002. The above pointed out high values during the stated months can be an obvious demonstration of human activities and/or industrial pollution, during the cited periods.

Concerning the mean values for copper concentrations in all the stations with all the months, the levels were altered from 59 ± 39 to 79 ± 47 µg L^{-1}. Nevertheless, the range of the mean values in all the stations per month ranged from 34 ± 34 to 122 ± 31 µg L^{-1}. Both these ranges were lower than the WHO guideline for domestic water of 1000 µg L^{-1}.[19] Awofolu *et al.*[22], in their investigation mentioned above, determined the concentration mean value for copper to be 387 ± 2. This level is much lower than the South African guideline for copper in domestic water supply of 0–1660 µg L^{-1}.[23] Comparing the copper level mean value in Shatt Al-Hilla river of 77 ± 43 µg L^{-1} with that found in Tyume river of 387 ± 2 µg L^{-1} shows clearly that the former is much lower than the latter.

Pertaining to iron, the stated mean value of 60 ± 33 µg L^{-1} is lower than the WHO guideline for domestic water of 300 µg L^{-1}.[19] This reveals that, in view of Fe, Shatt Al-Hilla river is appropriate for domestic employment. Nevertheless, the high standard deviation of 33 µg L^{-1} demonstrated the fluctuation of some values. Indeed, two high values of 70 and 100 µg L^{-1} have been recorded for stations 1 and 2 respectively, during November 2001. In addition, four values of 76, 75, 75 and 70 µg L^{-1} for stations 1, 2, 5 and 6 respectively, through December

2001 were observed. Besides, a value of 76 μg L^{-1} was noticed for station 1, during January 2002. Another value of 73 μg L^{-1} was obtained for station 1, throughout February 2002. Also, six values of 70, 100, 110, 70, 80 and 80 μg L^{-1} were observed for all the stations, *i.e.* 1, 2, 3, 4, 5 and 6 respectively, during March 2002. Another two values of 70 and 100 μg L^{-1} were recorded for stations 1 and 2 respectively, during June 2002. Finally, two values of 90 and 77 μg L^{-1} were obtained for stations 1 and 4 respectively, throughout September 2002.

Concerning iron concentration mean values for all the stations with all the months, the levels diverged between 46 ± 33 and 66 ± 35 μg L^{-1}. In addition, the mean values for all the stations per month were in the range 47 ± 35 to 85 ± 16 μg L^{-1}. Both the ranges were lower than the WHO guideline for domestic water of 300 μg L^{-1}.[19] Fatoki *et al.*[24] determined iron levels in the Umtata river, Eastern Cape, South Africa. The mean levels of iron in the river ranged between 100 and 4470 μg L^{-1} which exceeded the South African Target Water Quality Range (TQWR) of 100 μg L^{-1} for domestic water[23]. Moreover, these mean levels are much above that found in Shatt Al-Hilla river.

With regards to manganese, the cited mean value for the-metal of 36 ± 21 μg L^{-1} is lower than the WHO guideline for domestic water of 100 μg L^{-1}.[19] This reveals that, in consideration of iron, Shatt Al-Hilla river is appropriate for domestic use. Nevertheless, the high standard deviation of 21 μg L^{-1} demonstrated the fluctuation of some values. Actually, two values of 73 μg L^{-1} and 45 μg L^{-1} were noticed for stations 2 and 4 respectively, during November 2001. Another one value of 46 was recorded for station 3 throughout January 2002. Also, another one value of 45 was observed for the station during February 2002. Besides, four values of 57, 47, 57 and 47 μg L^{-1} were detected for stations 1, 2, 3 and 4 during March 2002. In addition, three values of 43, 43 and 52 μg L^{-1} were obtained for stations 1, 2 and 5 respectively, through April 2002. Moreover, three values of 53 and 70 and 56 μg L^{-1} were noticed for stations 2, 3 and 6 respectively, during July 2002. Finally, five values of 55, 49, 70, 54 and 53 μg L^{-1} were obtained, respectively, throughout September 2002. All these recorded high values during the corresponding periods reveal a clear evidence for man-induced and/or industrial pollution during the stated periods.

Relating to manganese, the range of the mean values of the concentration of the metal in all the stations with all the months, varied from 31 ± 19 to 40 ± 19 μg L^{-1}. On the other hand, the mean values of all of the stations per month ranged from 13 ± 8 to 54 ± 10 μg L^{-1}. Both ranges disclose once again the depression in the Mn levels in Shatt Al-Hilla river.

Pertaining to molybdenum, the mentioned mean value for the metal of 283 ± 217 μg L^{-1} is much greater than the WHO guideline for domestic water of 70 μg L^{-1}.[19] This reveals that, in consideration of molybdenum, Shatt Al-Hilla river is inappropriate for domestic use. Moreover, the high standard deviation of 217 μg L^{-1} demonstrated the vacillation of some values. Indeed, five values of 480, 635, 470, 660 and 940 μg L^{-1} were observed for stations 1, 3, 4, 5, 6, respectively, during December 2001. In addition, four values of 450, 450, 360 and 420 were detected for stations 1, 2, 3 and 4 through January 2002. Besides, five values of 320, 350, 330, 340 and 420 μg L^{-1} were recorded for stations 1, 2, 4, 5 and 6 during March 2002. Furthermore, one value of 390 μg L^{-1} was noticed for station 1, throughout April 2002. Moreover, one value of 350 μg L^{-1} was observed for the station 6 in July 2002. Lastly, three values of 350, 365 and 375 μg L^{-1} were noted for stations 2, 3 and 4 during August 2002. All these obtained elevated values suring the correlated periods reveal obviously the man-induced and/or industrial pollution throughout the declared periods.

Concerning the mean value range for molybdenum concentrations in all the stations through all the months, it diverged between 231 ± 202 to 342 ± 287 μg L^{-1}. However, the mean value range of all the stations per month was from 15 ± 1 to 581 ± 21 μg L^{-1}. Both the ranges disclose, regarding Mo, the highly elevated levels of this metal, confirming the unsuitability of water for domestic usage.

Regarding to nickel, the mentioned mean value of 50 ± 27 μg L^{-1} exceeded highly the WHO guideline for domestic water of 20 μg L^{-1}.[19] This demonstrated, regarding nickel, the unsuitability of Shat-Al-hilla river water domestically. In addition, the high standard deviation of 27 μg L^{-1} confirms the unsteadiness of the values. Actually, one value of 86 was recorded for station 2 during November 2001. Another four values of 67, 65, 58 and 61 μg L^{-1} were detected for stations 2, 4, 5 and 6 through January 2002. In addition, one value of 57 μg L^{-1} was observed for station 1, during February 2002. Furthermore, six values of 55, 82, 83, 59, 60 and 64 μg L^{-1} were noticed, for all the stations, respectively, throughout March 2002. Besides, one value of 62 μg L^{-1} was obtained for station 2 in April 2002. Again, five values of 75, 75, 63 and 114 μg L^{-1} were perceived, through July 2002. Moreover, two values of 66 and 64 μg L^{-1} were found for stations 1 and 2 throughout August 2002. Finally, five values of 60, 69, 65, 59 and 63 μg L^{-1} were recognized for the stations 1, 2, 4, 5 and 6 during September 2002. All these values through the corresponding periods show the man-induced and/or industrial pollution of Shatt Al-Hilla river water.

Concerning the mean value range for nickel concentrations in all the stations with all the months, it varied from 41 ± 27 to 61 ± 33 μg L^{-1}. Besides, the mean value for all the stations per month was of the range 30 ± 12 to 85 ± 33 μg L^{-1}. Both ranges were exceeding the above cited WHO guideline for domestic water of 20 μg L^{-1},[19] showing once again that, with regard to nickel, Shatt Al-Hilla river water is inappropriate for domestic utilization. Awofolu *et al.*[22] found the concentration of nickel, in Thyume river, South Africa, to fall within the range 201 ± 3 to 1777 ± 2 μg L^{-1}, which was much higher than the WHO guideline for domestic water of 20 μg L^{-1}.[19] These ranges exceed deeply the mean value obtained for Shatt Al-Hilla river of 50 ± 27.

Regarding selenium, the mentioned mean value of 35 ± 20 μg L^{-1} exceeded highly the WHO guideline for domestic water of 10 μg L^{-1}.[19] This demonstrated, with regard to selenium, the inappropriateness of Shatt Al-Hilla river water domestically. In addition, the high standard deviation of 20 μg L^{-1} confirms the unsteadiness of the values. Indeed, one value of 70 μg L^{-1} was noticed for station 2 during November 2001. Another value of 70 μg L^{-1} for the same station was recorded through December 2001. In addition, two values of 70 and 70 μg L^{-1} for stations 3 and 5, respectively, were detected throughout January 2002. Furthermore, two values of 51 and 45 μg L^{-1} were obtained for the stations 1 and 3, respectively, during February 2002. Another four values of 44, 40, 50 and 41 μg L^{-1} were found for stations 1, 2, 5 and 6 respectively, during April 2002. Moreover, four values of 49, 42, 46 and 41 μg L^{-1} for stations 1, 2, 3 and 5, respectively, were observed during August 2002. Finally, four values of 47, 47, 46 and 51 μg L^{-1} for stations 2, 4, 5 and 6 were recorded in September 2002. These high values during the corresponding periods demonstrate the human and/or industrial activities toward the contamination of Shatt Al-Hilla river water.

With regard to the mean values of selenium in all the stations with all the months, the values ranged between 31 ± 18 and 41 ± 24 μg L^{-1}. In addition, the mean value range of all the stations per month was 17 ± 26 to 45 ± 5 μg L^{-1}. Both the ranges exceeded the WHO guideline for domestic water of 10 μg L^{-1}[19], ascertaining, with regard to selenium, the unsuitability of Shatt Al-Hilla river water for domestic use. In addition, selenium is well known to have substantial, potential, rapid and severe impacts on fish populations, when its level becomes ≥ 1 μg L^{-1}. Lemly[25] investigated the pollution of Belews Lake, USA, by selenium. The results showed that the lake is the most extensively documented case of selenium poisoning in fresh water fish. Concentrations of selenium in the lake were recognized to be at an average 10 μg L^{-1}, which is highly elevated compared with the South African Target Water Quality Range (TQWR) guidelines for aquatic ecosystem of 2 μg L^{-1}.[26] Comparing the found concentration average with that obtained in Shatt Al-Hilla river of 35 ± 20 revealed that the latter was more polluted than the former.

Regarding vanadium, the mentioned mean value of 1314 ± 950 μg L^{-1} exceeded highly the tentative South African Target Water Quality Range (TWQR) guideline of 100 μg L^{-1} in river water for domestic employment[26]. This demonstrated, regarding vanadium, the inappropriateness of Shatt Al-Hilla river water domestically. In addition, the high standard deviation of 950 μg L^{-1} showed an instability of vanadium levels. In fact, three high values of 1950, 1680 and 1480 μg L^{-1} for stations 1, 2 and 4, respectively, were detected during March 2002. In addition, six high values of 1490, 1410, 1460, 1710, 2850 and 2750 μg L^{-1} for stations 1, 2, 3, 4, 5 and 6 respectively, were found during April 2002. Furthermore, four high values of 2000, 1500, 1750 and 1550 μg L^{-1} were recorded for stations 1, 2, 3 and 6, respectively, during July 2002. Moreover, four values of 2480, 2400, 3200 and 2650 μg L^{-1} for stations 3, 4, 5 and 6 respectively, were noticed through August 2002. Finally, five high values of 2300, 1940, 1600, 2230 and 2840 μg L^{-1}, respectively, were observed throughout September 2002. The above stated high values throughout the mentioned periods have been ascribed to industrial as well as man-induced activities. As regards the mean values of vanadium concentrations in all the stations with all the months, the values ranged between 830 ± 753 and 1240 ± 1204 μg L^{-1}. Furthermore, the mean values in all the stations per month ranged between 63 ± 155 and 2220 ± 774 μg L^{-1}. Both the ranges reveal once again, regarding vanadium, the unsuitability of Shatt Al-Hilla river water for domestic employment. Most surface fresh waters contain less than 3 μg L^{-1} of vanadium.[27] Zhang and Zhou[28] reported the concentrations of dissolved V in the source area of the Yangtze river in China to range from 0.02 to 0.46 μg L^{-1}. A research has been accomplished on the St Lawrence river water, St. Lawrence region, which is the most populated and developed area in Canada. The results demonstrate that vanadium concentrations in the river water area were 0.4, 0.8 and 2 μg L^{-1} for the Great Lakes, Ottawa river and

Quebec city region, respectively[29]. The highest reported levels for vanadium were in the surface waters in the area of Mount Fuji in Japan. Two springs had 14.8 and 16.4 $\mu g\ L^{-1}$ and five river samples showed between 17.7 and 48.8 $\mu g\ L^{-1}$.[27]

Concerning zinc, the cited mean value of 70 ± 84 $\mu g\ L^{-1}$ was much lower than the WHO guidelines for domestic water of 5000 $\mu g\ L^{-1}$.[19] Hence, relating to zinc, Shatt Al-Hilla river water is quite appropriate for domestic utilization. Nevertheless, the high standard deviation of 84 $\mu g\ L^{-1}$ indicates the unsteadiness of the detected levels. Actually, six values of 355, 180, 240, 185, 160 and 165 $\mu g\ L^{-1}$ were detected for stations 1, 2, 3, 4, 5 and 6, respectively, through December 2001. Moreover, another six values of 170, 210, 225, 215, 325 and 170 $\mu g\ L^{-1}$ for stations 1, 2, 3, 4, 5 and 6, respectively, were noticed for January 2002. Consequently, the above stated levels during the accompanied periods, point toward man-induced as well as industrial pollution of Shatt Al-Hilla river water. Pertaining to the range of levels, the mean values for zinc in all the stations through all the months varied from 50 ± 63 to 73 ± 109 $\mu g\ L^{-1}$. On the other hand, the mean value range of all the stations per month changed from 0 to 219 ± 57 $\mu g\ L^{-1}$. Both the ranges were much less than the WHO guidelines for domestic water of 5000 $\mu g\ L^{-1}$, demonstrating the suitability of Shatt Al-Hilla river water for domestic use. Awofolu *et al.*[22] determined, among other elements, the mean value range of zinc in the Tyume river water, South Africa, to vary from 97 ± 5 to 431 ± 2 $\mu g\ L^{-1}$. The TWQR of 3000 $\mu g\ L^{-1}$ for domestic use shows that no detrimental effects were expected from the domestic usage of the river water[23]. Comparing these values with those observed in Shatt Al-Hilla river water of 70 ± 84 $\mu g\ L^{-1}$ shows that Tyume river water is more polluted with zinc than Shatt Al-Hilla river.

To perform a comparison among the stations with regard to all the studied parameters, the results were statistically analyzed, using completely randomized design (CRD). The least significant difference (LSD) has been obtained with a probability of 0.01 and 0.05. In addition, the *t*-test was utilized for a comparison among the different months of the year for each of the studied parameters. No significant differences among the stations have been noticed within all the studied parameters.

With regard to the comparison among the months, significant differences were observed in all the stations with a probability level of 0.05 for all the parameters except selenium, vanadium, zinc and the pH for station 1; cobalt and pH for station 2; manganese, zinc and pH for station 3; iron and zinc for station 4; molybdenum, iron and zinc for station 5 and cobalt and zinc for station 6.

Furthermore, the correlation coefficient (R), among all the studied parameters, was calculated. The results have shown the existence of a direct significant relation between vanadium and the total hardness, whereas an inverse relation was noticed with chromium, iron. Another direct relation was obtained between cobalt and nickel. Regarding chromium, a direct relation was detected with iron, whilst an inverse relation was seen with vanadium, water temperature, pH and total hardness. Concerning copper, the element correlates directly with molybdenum and inversely with cobalt. However, iron was found to have direct relation with chromium and an inverse one with vanadium, water temperature and total hardness.

As regards manganese, the element correlates directly with nickel and vanadium and inversely with zinc. However, vanadium was found to correlate directly with copper, zinc and pH and inversely with selenium. In addition, nickel was correlated directly with cobalt and manganese and inversely with pH. Vanadium was demonstrated to have direct relation with water temperature, pH and total hardness, whereas it had an inverse relation with zinc.

The water temperature was found to correlate directly with pH. Finally, the pH had direct relation with total hardness. The correlations of the measurements are shown in Table-4.

TABLE-4

THE CORRELATIONS OF THE MEASUREMENTS

Elements	Relation type	R-value	Probability level
1. Chromium			
Cadmium	Inverse	0.40	0.05
Iron	Direct	0.58	0.01
Mercury	Direct	0.33	0.05
Vanadium	Inverse	0.48	0.01
Temperature of water	Inverse	0.58	0.01
pH	Inverse	0.45	0.01
Total hadness	Inverse	0.33	0.05
2. Cobalt			
Copper	Inverse	0.36	0.05
Mercury	Inverse	0.59	0.01
Nickel	Direct	0.50	0.01
3. Copper			
Cobalt	Inverse	0.36	0.05
Molybdenum	Direct	0.46	0.01
4. Iron			
Cadmium	Inverse	0.50	0.01
Chromium	Direct	0.58	0.01
Lead	Direct	0.50	0.01
Vanadium	Inverse	0.42	0.05
Temperature of water	Inverse	0.57	0.01
Total hardness	Inverse	0.62	0.01
5. Manganese			
Mercury	Inverse	0.53	0.01
Nickel	Direct	0.53	0.01
Lead	Direct	0.42	0.01
Vanadium	Direct	0.44	0.01
Zinc	Inverse	0.44	0.01

Elements	Relation type	R-value	Probability level
6. Molybdenum			
Copper	Direct	0.46	0.01
Selenium	Inverse	0.46	0.01
Zinc	Direct	0.51	0.01
pH	Direct	0.41	0.05
7. Nickel			
Cobalt	Direct	0.50	0.01
Manganese	Direct	0.53	0.01
Mercury	Inverse	0.48	0.01
Lead	Direct	0.50	0.01
8. Selenium			
Molybdenum	Inverse	0.46	0.01
9. Vanadium			
Zinc	Inverse	0.63	0.01
Temperature of water	Direct	0.79	0.01
pH	Direct	0.45	0.01
Total hardness	Direct	0.39	0.05
10. Temperature of water			
pH	Direct	0.56	0.01
Total hardness	Direct	0.72	0.01
11. pH			
Total hardness	Direct	0.56	0.01

Regarding the significant differences, chromium demonstrated no significant differences in its concentration among the six stations, whilst all the stations demonstrated significant differences with a probability level of 5.1%, with the variation of the months. Likewise, cobalt showed no significant differences in its concentration among the six stations. However, stations 1, 3, 4 and 5 showed significant differences with variation of the months with a probability level of 5.1%. Nevertheless, no significant differences were obtained in stations 2 and 6.

Also, no significant differences were revealed in the concentration of copper among the six stations, whereas and because of the variation of the months, stations 1, 2, 3, 4 and 5 showed significant differences with a probability level of 5.1%. On the other hand, station 1 revealed significant differences with a probability level of only 5.0%.

With regard to iron, no significant differences in the concentration of the element have been obtained among the six stations. However, variation of the months led to significant differences in stations 2, 3 and 6 with a probability level of 5.1%, while station 1 showed significant differences with a probability level of only 5.0%. Nonetheless, no significant differences were noticed in the stations 4 and 5.

Concerning manganese, no significant differences in the concentration of the element have been demonstrated among the six stations, whereas, with the variation of the months, stations 1, 4 and 5 demonstrated significant differences with a probability level of 5.1%. However, stations 2 and 6 disclosed significant differences with a probability level of only 5.0%, whilst station 3 showed no significant differences with the variation of the months.

Pertaining to molybdenum, no significant differences in the concentration of the element were observed among the six stations, whereas significant differences among the months in stations 1, 2, 3 and 6 with a probability level of 5.1%. However, significant differences with a probability level of 5% was obtained in station 4, whereas station 5 showed no appreciable significant difference through the variation of months.

Relating to nickel, no significant differences in the concentration of the element were observed among the six stations, while significant differences with the variation of the months were observed in stations 2, 4, 5 and 6 with a probability level of 5.1%. On the other hand, stations 3 and 4 disclosed significant differences with a probability level of only 5.0%.

Moreover, selenium demonstrated no significant differences in the concentration of the element among the six stations, whereas significant differences with a probability level of only 5.1% were obtained in stations 2, 3, 4, 5 and 6 with a probability level of 5.1%. However, no significant differences were observed with variation of the months.

Additionally, vanadium showed no significant differences in the concentration of the element among the six stations. On the other hand, variation of months showed significant differences with a probability level of 5.1% in stations 2, 3, 4, 5 and 6. However, no significant differences were shown in station 1.

Furthermore, zinc has not demonstrated any significant differences in the concentration of the element among the six stations. However, station 2 revealed significant differences with a probability level of only 5.0%, while no significant differences were obtained in stations 1, 3, 4, 5 and 6.

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

Finally, concerning the pH no significant differences in the concentration of the elements have been obtained among the six stations. Nevertheless, with the variation of the months, station 6 demonstrated significant differences with a probability level of 5.1%, whereas stations 4 and 5 showed significant differences with a probability level of only 5.0%. Yet, no significant differences have been obtained in stations 1, 2 and 3.

REFERENCES

1. U. Forstner and G. Wittmann, Metal Pollution in the Aquatic Environment, 2nd Edn., Springer-Verlag, New York (1981).
2. J.P. Riley and R. Chester, Introduction to Marine Chemistry, Academic Press, London (1971).
3. B. Hart and S. Davies, Physicochemical Form of Trace Metals and the Sediment-Water Interface, in: H.L. Golterman (ed.), Interaction between Sediment and Fresh Water, Junk Publ., The Hague (1977).
4. A. Viarengo, *Mar. Poll. Bull.,* **16**, 153 (1985).
5. H. Bowen, Trace Elements in Biochemistry, Academic Press, Inc., New York (1966).
6. G. Phillips and R. Russo, *U.S.EPA.*, 60013–78 (1978).
7. B. Milne, in: C.A. Burtis and E.R. Ashwood (Eds.), Textbook of Clinical Chemistry, W.B. Saunders Company, Tokyo-London, Ch. 30, p. 1029 (1999).
8. K. Teo and J. Chen, *Anal. Chim. Acta*, **434**, 325 (2001).
9. A. Viarengo, M. Pertica., G. Mancinell, R. Capell and M. Orunesu, *Mar. Environ. Res.,* **4**, 145 (1981).
10. K. Simkiss, M. Taylor and A.Z. Mason, *Mar. Biol. lett.,* **3**, 187 (1982).
11. W.J. Bettger and B.L. O'dell, *Life. Sci.,***28**, 1425 (1981).
12. E.F. Pane, J.G. Richards and C.M. Wood, *Aquat. Toxicol.*, **63,** 65 (2003).
13. M. Rayman, *Lancet,* **15**, 356 (2000).
14. J. Alabaster and R. Lloyd, Water Quality Criteria for Fish, 2nd Edn.,Butterworths, London, (1980).
15. A. Medzini, The Euphrates: A Shared River, SOAS Water Research Group of the School of Oriental and African Studies, University of London (2001).
16. A. Wolf, Conflict and Cooperation along International Waterways, Water Policy, p. 251 (1998).
17. The Mid-year Report, Administration of Al-Hindiya Dam Irrigation (1992).
18. Canadian Drinking Water Quality Guideline (April 1996).
19. Guidelines for Drinking-water Quality, World Health Organization, Geneva, 3rd Edn., Vol. 1 (2004).
20. Department of Water Affairs and Forestry, South African Water Quality Guidelines, Agricultural Use: Livestock Watering, Vol. 5, 2nd Edn., DWAF, Pretoria (1996d).
21. M. Gulfraz, T. Ahmad and H. Afzal, *Online J. Bio. Sci.,* **1,** 414 (2001).
22. O.R. Awofolu, Z. Mbolekwal, V. Mtshemlal and O.S. Fatoki, *Water SA,* **31,** 87 (2005).
23. Department of Water Affairs and Forestry, Water Quality Guidelines: Domestic Use, Vol. 1, 2nd Edn., DWAF, Pretoria (1996a).
24. A.D. Lemly, *Human Ecol. Risk Assess.*, **5**, 1139 (1999).
25. Department of Water Affairs and Forestry, South African Water Quality Guidelines: Field Guide, Vol. 8, 1st Edn., DWAF, Pretoria (1996c).
26. T. Hamada, High Vanadium Content in Mount Fuji Groundwater and Its Relevance to the Ancient Biosphere, in: J. Nriagu (Ed.), Vanadium in the Environment, Part 1: Chemistry and Biochemistry, John Wiley & Sons, New York, NY, p. 97 (1998).
27. L. Zhang and K. Zhou, *Sci. Total Environ.*, **125**, 391 (1992).
28. St. Lawrence Center, State of the Environ. Report on the St. Lawrence River, Montreal, Quebec Region, Canada, Vol. 1 (1996).

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