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Levels of Heavy Metals Pollution in the Aquatic Environment of Basra City, Iraq

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Abstract This study aims to determine levels of heavy metals in the waters of Shatt Al-Arab river and its creeks and in the tap waters, and to analyze the spatial and seasonal variability in these levels, as well as to evaluate their hazards on public health in terms of the recommended exposure levels of these pollutants.

Water samples were collected from different stations within the urban area of Basra City during 2009. The obtained results have been shown that heavy metals levels in the aquatic environment of the study area were, in general, both spatially and seasonally varied; it were high during winter more than other seasons at several sampling stations. As well, a minimum and maximum of the recorded values of studied elements were ranged as follows: Fe were 0.90-9.18mg/l, Cu were 0-0.46mg/l, Pb were 0-0.72mg/l, Co were 0-0.89mg/l, and Ni were 0-1.84mg/l. The recorded levels of heavy metals, hence, represent a pollution to the aquatic environment of the study area, which expose a serious hazard to public health.

Key Words Heavy metals, Aquatic environment, Water, Pollution.

Introduction

Natural waters contamination is a worldwide distributed problem which deserves large attention not only due to its environmental hazardous effects but also for the risks to the human health as well as the economical damages it produces. Between the wide diversity of pollutants affecting water resources heavy metals receive particular concern considering their strong toxicity even at low concentrations. The occurrence of heavy metals in water bodies can be of natural origin (i.e., eroded minerals within sediments, leaching of ore deposits, and vulcanism extruded products) or for anthropogenic one (i.e., solid waste disposal, industrial or domestic effluents, harbor channels dredging) (Marcovecchio *et al*., 2007).

Most heavy-metal contamination stems from high-temperature combustion sources, such as coal-fired power plants and solid-waste incinerators. Local metal sources may include metal-plating industries and other metal industries. The use of leaded gasoline has led to global lead pollution even in the most pristine environments, from arctic ice fields to alpine glaciers. The metal fluxes from point sources have been strictly regulated, and the introduction of unleaded gasoline has taken a major lead source away. Several sites with severe heavy-metal pollution have become Superfund sites, most of them still under study for decontamination. Site decontamination can be done with large-scale soil removal and metal stripping, or through more gradual methods, like phytoremediation. Nonetheless, even today metals are delivered from the atmosphere to the landscape (Varekamp, 2004).

The heavy metals, which include copper (Cu), zinc (Zn), lead (Pb), mercury (Hg), nickel (Ni), cobalt (Co), iron (Fe) and chromium (Cr), are common trace constituents in the earth crust. Their concentrations in the ambient environment have increased dramatically since the Industrial Revolution (Varekamp, 2004).

It has been largely recognized that heavy metal concentrations are much higher in urban or industrial areas than in wild ones. Consequently the possibility of incorporation of heavy metals into drinking water or trophic webs exits, and so the potentially generation of deleterious effects on human populations.

Moreover the toxicity of heavy metals can be significantly increased due to synergistic effects within natural systems. In addition, and considering the average long-life of these elements, their persistence and potential transformation to more toxic compounds must be addressed (Marcovecchio *et al*., 2007).

The daily intake of these metals is often toxic or lethal. Many heavy metals cause nervous-system damage, with resulting learning disorders in children. Ingestion of mercury can cause the severe breakdown of the nervous system, and metals such as lead and nickel can cause autoimmune reactions (Varekamp, 2004).

Even though the natural levels of heavy metals are well known those from aquatic ecosystems have significantly increased in the last decades simultaneously with the high development of industrial activities and urban developments. So, the necessity to develop analytical methods allows to detect and quantify extremely low levels of heavy metals in natural waters (which could be quiet dangerous for both aquatic biota and human health) that is strongly remarked (Marcovecchio *et al*., 2007). Therefore, existence of heavy metals in environment often considered as an indicator on that contamination is occurring (Sanchez *et al*., 2008).

Basra City (the study area) is one of the largest urban centers located in Southeast Iraq at the point of 30º34N and 47º50E coordinate (see Fig.1). The various urban activities involved in the study area may be a source of heavy metals contamination. This study, hence, aims to determine levels of heavy metals in the waters of Shatt Al-Arab river and its creeks and in the tap waters, and to analyze the spatial and seasonal variability in these levels, as well as to evaluate their hazards on public health in terms of the recommended exposure levels of these pollutants.

Materials and Methods

Spatially, as shown in Fig.1 and Tab.1, water sampling stations were selected from Shatt Al-Arab river before entering into the urban area of Basra City (sample of No.1), and within the boundary of Basra City (sample of No.2), while other sampling stations represent in its creeks such as Rubat (sample of No.3), Khandak (sample of No.4), Ashar (sample of No.5), Khorah (sample of No.6), as well as Sewage Drain (sample of No.7). Tap water samples were also collected from different districts (samples of Nos.8,9,10, and11). Seasonally, the collection of water samples was carried out for four rounds according to seasonal variation in river water levels during winter, spring, summer, and autumn.

To determine the heavy metals, studied water samples were analyzed according to a procedure of Riely and Taylor (1968) and Sturgeon *et al.*,(1982). This procedure is described as follows: 50ml of water sample is taken, and 5ml of HNO_3 is added to it. Each of the sample is stored in a glass beaker with screw cap, and then put it up on a hot plate at a temperature of 80-100C^o, and must it take off upon the hot plate when it approaches to the boiling, then return it upon the hot plate again when the boiling is dropped. This process is repeated again and again until the studied water sample reach to the dryness and it precipitated as a white salt. After the digestion procedure is finished, the precipitated salt is dissolved by using a mixture of distilled water and a few drops of HCl (concentrated at 0.5) and the resulting solution has to be shaking by the hand until becoming a completely uniform solution. The solution is filtered through a 0.45µm filter, and then it's stored in a screw-cap bottle. Concentrations of trace metals in samples are usually determined by Atomic Absorption Spectrophotometer, AA 320N model, US made.

Results and Discussion

Five of heavy metals (Fe, Cu, Pb, Co, and Ni) has been discussed in the present study. The measured levels of these pollutants in the studied water samples are shown in Tab.1, the geographical analysis will be conducted in the terms of each metallic element, as follows:

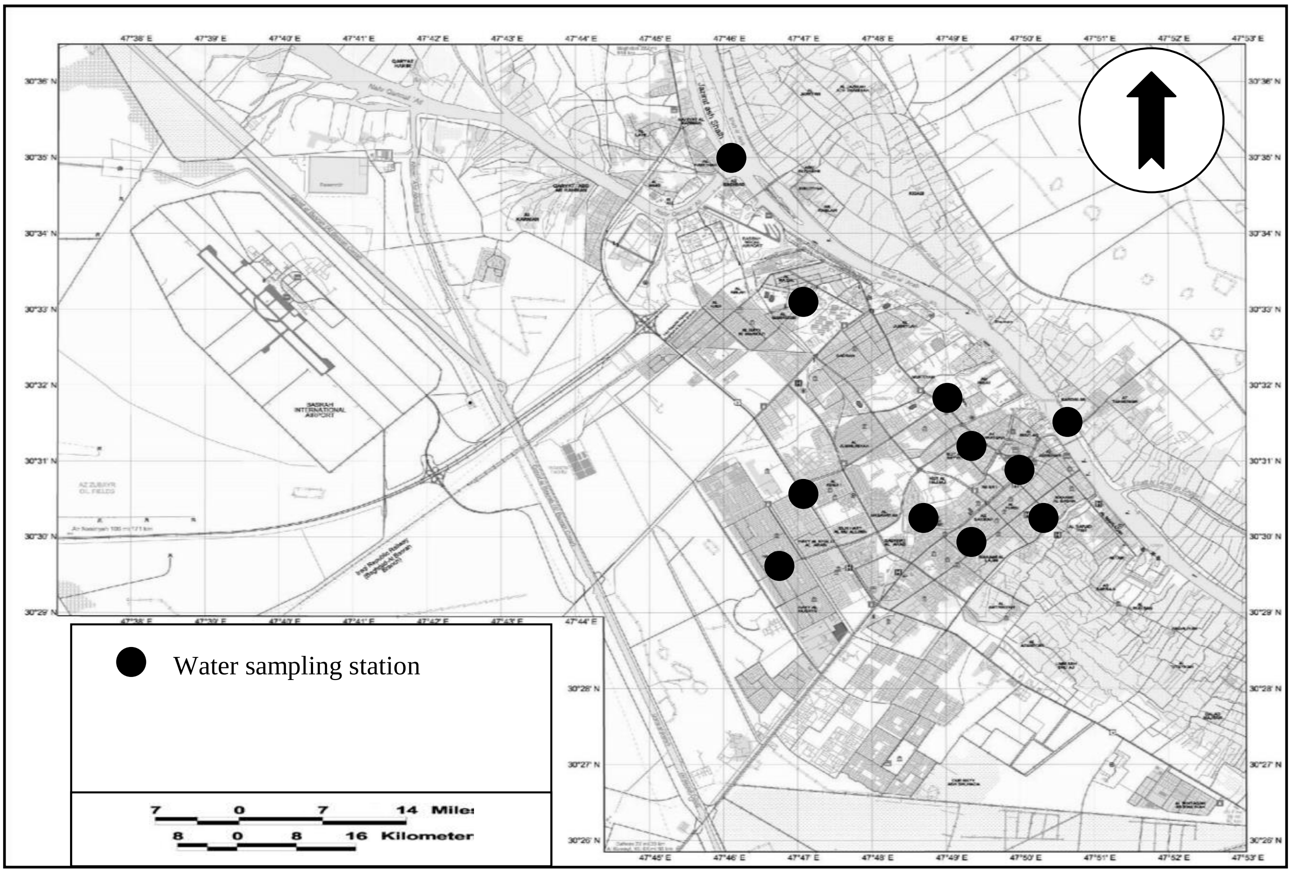

Figure 1: Map of the study area (Basra City) and sampling stations.

1- Iron (Fe): Iron metal had an atomic number and weight is 26 and 55.847, respectively. Iron is a common component of waters. Higher amounts of iron are found in the waters of peat moors where iron is bonded in complexes with humic substances and is kept in a stable colloid solution. During spring and autumn circulation, Fe(II) is dispersed in the whole water column and it oxidizes at the surface to Fe(III) due to the contact with dissolved oxygen and is hydrolysed (Tolgyessy, 1993).

As shown in Fig.2, Fe concentration in water sampling stations was spatially and seasonally varied. It is significantly increased in most of the studied sample stations during the winter and spring. Relatively low air temperature acts as chemical reactions is occurring and transforming the iron into another form or its concentration is diluted. Spatially, the highest levels lie in the Shatt Al-Arab river at a sampling station of Kornish (sample of No.2) rather than sampling station of Garmmatt (sample of No.1), indicating that water of Shatt Al-Arab river is affected by urban pollutants. As well, there were high levels in some creeks such as Rubat, Khandak, and Ashar respectively. It is interesting that there were high concentrations of Fe in tap water samples, particularly at Maqal, Hayyaniyah, and Baradithyah, this may be referred to oxidization and corrosion of pipelines, which give rise to increase of iron oxides in water supplies.

To standardize with the recommended exposure level of 0.3mg/l (Tolgyessy, 1993), demonstrates that concentrations of Fe in all sampling stations and periods were exceeded, as shown in Fig.2.

2- Copper (Cu): Copper metal had an atomic number and weight is 29 and 63.546, respectively. In surface waters the dissolved forms of copper are mostly complex compounds. Copper concentration, therefore, tends to oscillate in waters (Tolgyessy, 1993). Since copper is a relatively rare metal and its solubility in natural waters is limited, then industrial and urban contaminates can consider the major source to the presence of copper in aquatic environments (Feng *et al*., 2008).

Table 1: Concentrations of some heavy metals in water samples (in mg/l) at the study area during the four seasons of 2009.

NO.	Sampling Station	Winter					Spring				
		Fe	Cu	Pb	Co	Ni	Fe	Cu	Pb	Co	Ni
1	Shatt Al-Arab river, Garmmatt	3.78	0.17	0.54	0.74	0.93	2.82	0.07	0.17	0.30	0.22
2	Shatt Al-Arab river, Kornish	4.50	0.17	0.54	0.74	2.26	3.60	0.08	0.36	0.10	0.88
3	Rubat creek	4.68	0.21	0.54	0.89	1.84	9.18	0.15	0.20	0.40	0.50
4	Khandak creek	5.94	0.46	0.72	0.58	0.50	2.70	0.17	0.18	0.47	1.63
5	Ashar creek	6.30	0.29	0.72	0.84	0.50	3.24	0.12	0.20	0.44	1.73
6	Khorah creek	1.98	0.17	0.18	0.84	1.13	1.88	0.12	0.10	0.30	0.94
7	Sewage drain	1.44	N.D	N.D	0.37	0.37	3.96	0.17	0.18	0.47	1.13
8	Tap water, Maqal	3.60	0.21	0.54	0.63	1.63	3.90	0.38	0.20	0.20	0.40
9	Tap water, Al-Basrah Al-Qadimah	3.96	0.08	0.36	0.21	0.37	1.20	N.D	N.D	0.18	0.20
10	Tap water, Hayyaniyah	1.44	0.17	0.36	0.42	0.75	2.24	1.11	0.10	0.42	0.80
11	Tap water, Baradithyah	5.04	0.25	0.54	0.68	1.60	2.88	0.12	0.18	0.52	1.51

NO.	Sampling Station	Summer					Autumn				
		Fe	Cu	Pb	Co	Ni	Fe	Cu	Pb	Co	Ni
1	Shatt Al-Arab river, Garmmatt	1.80	N.D	0.54	0.37	0.12	1.98	N.D	0.36	0.52	1.38
2	Shatt Al-Arab river, Kornish	1.08	N.D	0.36	0.21	0.37	1.62	0.04	0.18	0.74	1.13
3	Rubat creek	1.08	0.08	0.36	0.31	0.88	1.26	N.D	N.D	0.42	0.75
4	Khandak creek	1.80	0.04	0.36	0.37	0.75	0.90	N.D	0.36	0.37	0.12
5	Ashar creek	3.60	0.04	0.18	0.52	0.12	1.98	N.D	0.18	0.52	0.12
6	Khorah creek	1.08	0.12	0.18	0.84	1.63	1.08	N.D	0.54	0.84	N.D
7	Sewage drain	1.62	0.08	0.18	0.37	0.50	1.62	N.D	0.36	0.52	0.75
8	Tap water, Maqal	1.44	0.04	N.D	0.31	0.37	1.98	0.04	0.18	0.63	0.37
9	Tap water, Al-Basrah Al-Qadimah	2.34	0.08	0.36	N.D	N.D	3.06	0.08	N.D	0.21	0.37
10	Tap water, Hayyaniyah	0.90	N.D	N.D	0.31	0.12	1.44	N.D	0.18	0.31	0.12
11	Tap water, Baradithyah	1.26	0.04	0.36	0.31	0.88	1.62	0.12	0.36	0.63	0.37

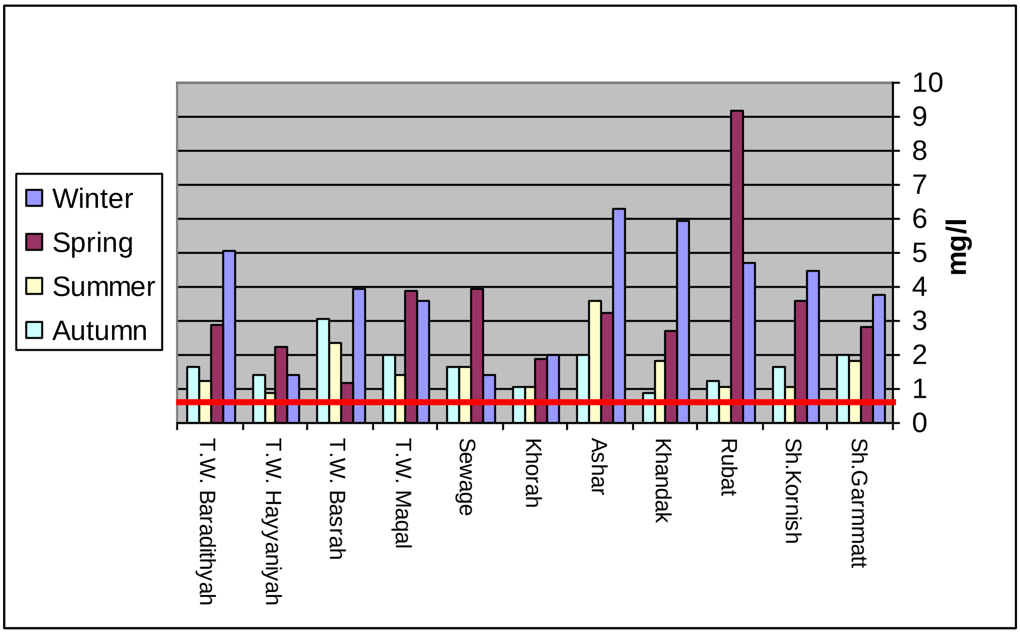

Figure 2: A graphic representation of concentrations of Fe (in mg/l) in waters of the study area, 2009.

Fig.3 reveals that there were significant concentrations of Cu during winter and spring seasons at most of sampling stations, while those concentrations during summer and autumn were so low. This seasonal variation is may ascribe to elevated air temperature and high rate of evaporation during summer and autumn seasons, which give rise to dilution in Cu concentration in waters. In particulate, highest levels of Cu were at creeks (Rubat, Khandak, Ashar, and Khorah). In addition, the recorded levels in tap water samples were markedly higher, may be referred to corrosion involved in pipelines as well as pollutants discharged from water supply stations.

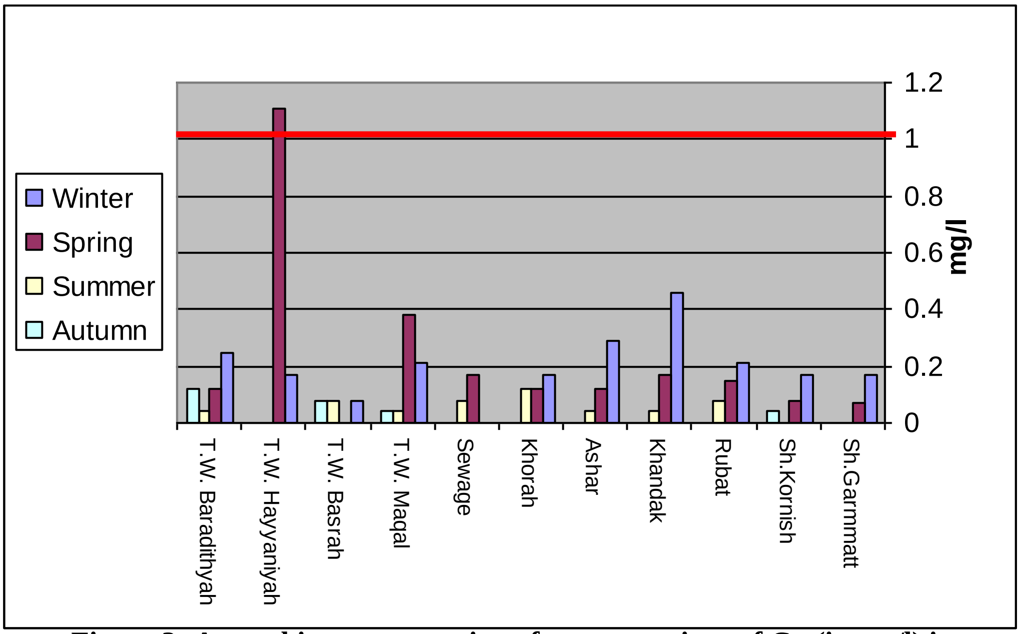

Figure 3: A graphic representation of concentrations of Cu (in mg/l) in waters of the study area, 2009.

Copper is not so poisonous for humans as was assumed in the past. However, a concentration of 1-5mg/1 causes a very unpleasant taste of water. Compounds of copper are fairly toxic to fish (Tolgyessy, 1993). Accordingly, Cu concentrations do not exceed the recommended exposure levels (1mg/l), thus the recorded levels to be considered safer in this respect, except the Cu concentration at a sampling station of Hayyaniyah (sample of No.10) that is reached to 1.11mg/l (see Fig.3).

3- Lead (Pb): Lead metal had an atomic number and weight is 82 and 207.19, respectively. Artificial and increasingly important sources of lead are exhaust gases of motor vehicles, which contain degraded products of tetraethyl lead. Via atmospheric precipitation, lead is introduced into surface waters. Since it has a high accumulation coefficient its major portion is removed from surface waters by sorption on the bottom sediments. In natural waters, Pb2+ and [PbCO,(aq)]' are the significant soluble forms. In the alkaline region also [Pb(C0),I2-, [Pb(0H),(aq)lo and [PbOH]' complexes are to be considered. In waters with a high concentration of sulphates the [PbS04('aq)]' complex is also important. In addition, at high concentrations of chlorides different chloro complexes must also be taken into consideration (Tolgyessy, 1993).

As shown in Fig.4, there were high concentrations of Pb in studied water samples, particularly during winter at most of sampling stations. This is associated with lower air temperature which, in turn, causes a reduction in evaporation and then increase of Pb concentration in waters. However, levels of Pb were significant in sampling stations of both Shatt Al-Arab river and its creeks, though this is varied from one site into another. Pb concentrations in tap water samples of Maqal and Baradithyah (samples of Nos.8 and 11, respectively) were higher than those in Al-Basrah Al-Qadimah and Hayyaniyah (samples of Nos.9 and 10, respectively).

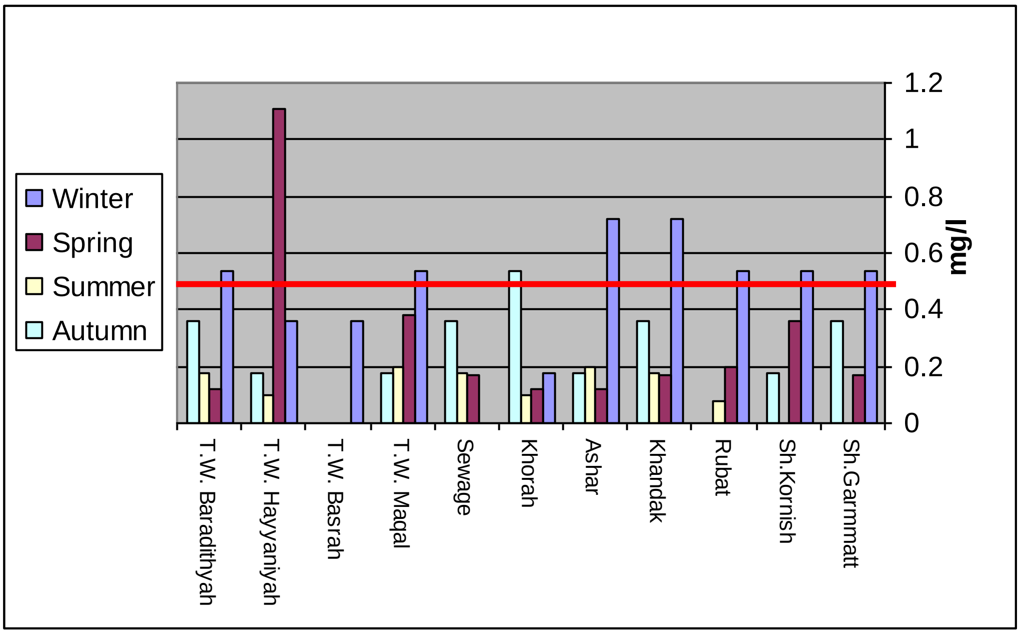

Figure 4: A graphic representation of concentrations of Pb (in mg/l) in waters of the study area, 2009.

Lead is a traditional poison and it is very dangerous when present in waters. Therefore, no lead pipes are nowadays used for the distribution of drinking water. Lead poisoning from environmental exposure is thought to have caused mental retardation in many children. Mild lead poisoning causes anemia. The victim may have headaches and sore muscles, and may feel generally fatigued and irritable (Yu, 2005). The maximum concentration of lead in drinking water recommended by the World Health Organization is 0.5 mg/l (Tolgyessy, 1993).

In compassion with the present data, it is clear that Pb concentrations exceeded the WHO recommended exposure level, as in the water sampling stations of Shatt Al-Arab river, Rubat, Khandak, Ashar, Khorah, Maqal, and Baradithyah. Thus, it has to be careful when doing dealing with these waters because of poisoning by lead.

4- Cobalt (Co): Cobalt metal had an atomic number and weight is 27 and 58.933, respectively. Organically bonded cobalt occurs in the sludge from biological wastewater treatment plants in the form of vitamin B_{12} (Tolgyessy, 1993).

As shown in Fig.5, it was observed that Co levels in several selected sampling stations were elevated during winter and autumn in particular. This might be associated with the lowest rate of evaporation during winter increasing of Co concentration in water, as well as the effect of seawater wave procession during autumn. Spatially, Co concentration was high at the Khorah creek (sample of No.6) in particular, in comparing to other sampling stations. The organic nature of this creek's water and sewage effluents which are discharged into it is the likely reason behind those elevated values. In respect of tap water samples, sampling stations of Maqal and Baradithyah (samples of Nos.8 and 11, respectively) records the highest values, because of both takes its water supplies from Shatt Al-Arab river which is already contaminated by this metal.

The recommended exposure level of cobalt in drinking water is 0.5mg/l. Accordingly, almost all studied sampling stations, except for both sampling stations of Al-Basrah Al-Qadimah and Hayyaniyah (samples of Nos.9 and 10, respectively) being exposed to cobalt contamination (see Fig.5).

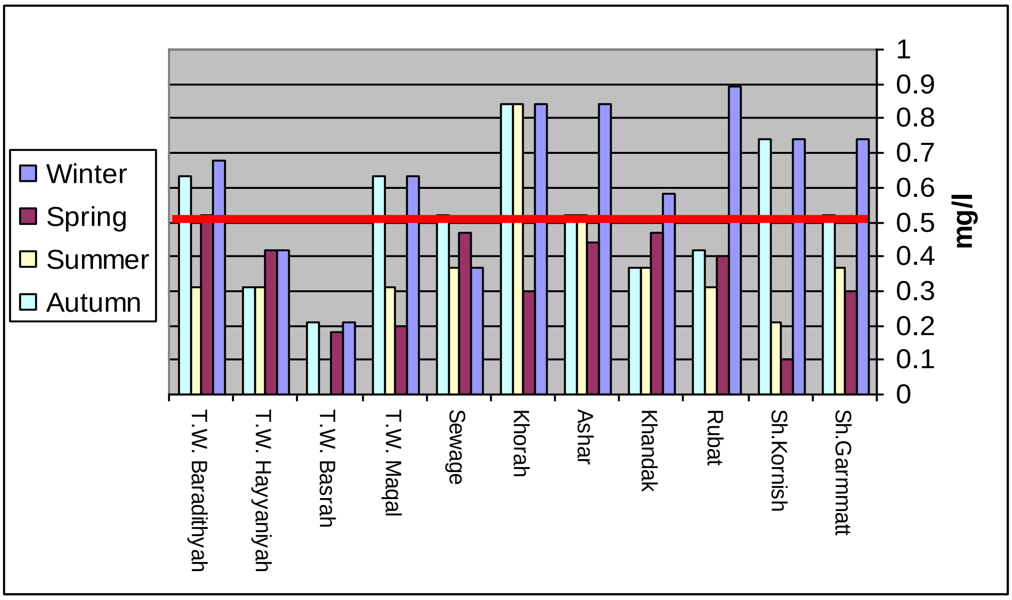

Figure 5: A graphic representation of concentrations of Co (in mg/l) in waters of the study area, 2009.

5- Nickel (Ni): Nickel metal had an atomic number and weight is 28 and 58.71, respectively. Nickel was largely ignored for industrial use until just before 1900, when the Mond carbonyl process was discovered as a way to remove the metal in a pure form from the mined ores. This process was the key to triggering concern for worker safety because part of it involved nickel carbonyl gas, Ni(CO)4, the most toxic form of the metal. Other forms of Ni, however, play an uncertain role in the safety of workers and the public. Overall demand for Ni has been increasing over time, mostly due to increasing stainless-steel production. Ni is used in approximately 250,000 industrial applications, and is used in the forms of nickel carbonate, nickel carbonyl, nickel chloride, nickel nitrate, nickel oxide, nickel sulfate, and nickel sulfide. Some applications include use in iron processing, nickel plating, and nickel–cadmium batteries. Nickel iron is used for electrical equipment, copper nickel is used as an anticorrosive for marine vessels and equipment, and nickel titanate is used as a pigment in paints. As Ni refineries increase production, the concern for this heavy, mobile metal and its effects on the environment also increases (Yu, 2005).

Nickel can enter natural waters primarily from wastewaters discharged from plants involved in the surface finishing of metals (Tolgyessy, 1993).

It was observed, as shown in Fig.6, that the measured concentrations of Ni were seasonally varied. These concentrations have been reached to the maximum value during the winter at sampling stations of Shatt Al-Arab river (Kornish), Rubat creek, Maqal, and Baradithyah (samples of Nos.2, 3, 8, and 11 respectively), and during spring at sampling stations of Khandak creek, Ashar creek, Sewage drain, and Hayyaniyah (samples of Nos. 4, 5, 7, and 10 respectively), while during summer at sampling station of Khorah (sample of No.6), and during autumn at a sampling station of Shatt Al-Arab river (Garmmatt) (sample of No.1). The greatest concentrations of Ni during winter and spring in particular, it might be due to the low rate of evaporation which is , in turn, associated with decrease in air temperatures during both these seasons, causing a further concentration of Ni in the waters. In the terms of spatial variability, a significant concentration of Ni which was recorded in Rubat creek and Shatt Al-Arab river at Kornish may be considered as an indication on exposing to this sort of pollutants.

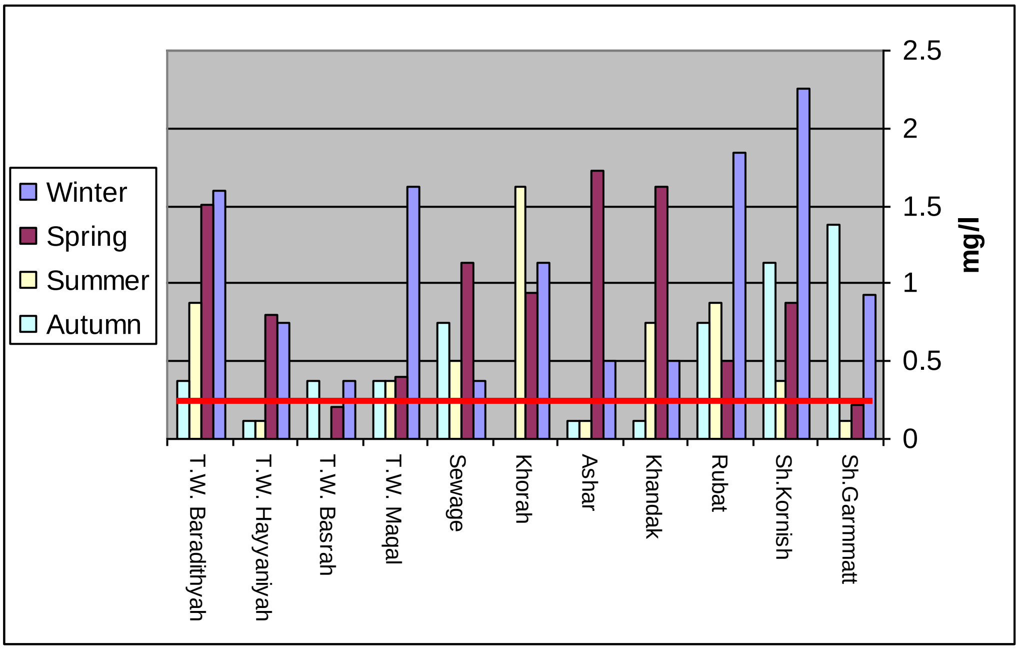

Figure 6: A graphic representation of concentrations of Ni (in mg/l) in waters of the study area, 2009.

The recommended exposure level of Ni in drinking water should be not exceed 0.2mg/l. By comparison between the recommended level and recorded levels, it demonstrates a big difference between the both values at all selected sampling stations and seasons, even in the case of tap water samples (see Fig.6). The water quality, therefore, in the study area is very dangerous in the terms of this contaminate. Studies (Yu, 2005) report that symptoms of contamination with nickel may include nasal boils, cysts, perforation of the nose, pharyngitis, sinusitis, and nasal polyps.

However, several previous research papers and studies (Al-Hashimi and Slaman,1985; Abaychi and Douabul,1985; Al-Sabah,2007; Al-Muddafr *et al*.,1992; Al-Saad *et al*.,1996; Al-Imarah and Al-Khafaji,1997; Al-Imarah *et al*.,2008), concluded that the waters of Shatt Al-Arab and its creeks exposed, to a some extent, to heavy metals pollution as a result of many sources of contamination. These research papers and studies reported, then, that levels of heavy metals are increasingly rising over time.

Accordingly, several specialized studies (Mostuafa,1985; Abaychi and Al-Adhub, 1987; Abaychi and Al-Obaidy,1987; Abaychi and Al-Saad,1988; Al-Saad and Al-Imarah,1997; Al-Khfaji,1997; Al-Khfaji *et al*.,1997a; Al-Khfaji *et al*.,1997b; Al-Imarah *et al.*,1997; Al-Saad *et al.*,1997; Al-Qarooni,2011) found that fishes such as *Cyprinus carpio*, *Tenualose illisha*, *B.sharpeyi*, *L.Subviridis*, and *N.nasus*, as well as other aquatic organisms such as crustaceans, phytoplankton, zooplankton, and algae, were contaminated with heavy metals.

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مستويات التلوث بالمعادن الثقيلة في البيئة المائية لمدينة البصرة، العراق

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المستخلص ترمي هذه الدراسة إلى تحديد مستويات المعادن الثقيلة في مياه نهر شط العرب وبعض الجداول المتفرعة عنه وتحديد مستوياتها في بعض عينات مياه الإسالة. كما تهدف إلى تحليل التباين المكاني والفصلي لتلك المستويات، فضلاً عن تقييم مدى خطورتها على الصحة العامة في ضوء معايير التعرض المسموح بها الخاصة بتلك الملوثات.

تم جمع عينات المياه من مواقع مختلفة ضمن مدينة البصرة خلال العام 2009. وبينت النتائج المستخلصة أن مستويات المعادن الثقيلة في البيئة المالية لمنطقة الدراسة كانت، في العموم، متباينة مكانياً وفصلياً على حد سواء؛ فقد كانت مرتفعة في أثناء الشتاء أكثر منه في الصيف في معظم المواقع. وأن أدنى وأعلى قيمة مسجلة للعناصر المدروسة كانت على النحو التالي: الحديد 0.90-9.18 ملغم/لتر، النحاس 0-0.46 ملغم/لتر، الرصاص 0-0.72 ملغم/لتر، الكوبلت 0-0.89 ملغم/لتر، والنيكل 0-1.84 ملغم/لتر. وتمثل معظم المستويات المسجلة تلوثاً للبيئة المائية في منطقة الدراسة وتشكل خطراً جدياً على الصحة العامة.

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