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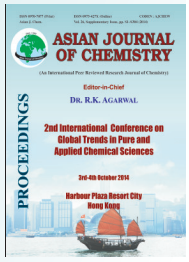

Seasonal Variation in Heavy Metals Contamination in Surface Water of Shatt Al-Hilla River, Babylon, Iraq

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In the present work, monitoring of monthly variations in the concentration of heavy metals (Pb, Ni and Fe) in Shatt Al-Hilla river water have been carried out during November 2011-October 2012 to study the extent of contamination of the river with these metals. Sampling was achieved from 14 selected study sites (most likely to be affected by pollutants). The technique of flame atomic absorption spectrometry was used to determine the concentration of heavy metals in the water samples. Results have shown wide variations in the heavy metals levels varying from high concentration of one of the metals at certain site to low content of other. A total of 168 surface water samples collected from Shatt Al-Hilla river in med of Iraq, were analyzed for Pb, Ni and Fe. The concentrations of the metals Pb, Ni and fewere detected in 100 % of the samples in the range of 0.030-16.090, 0.080-13.000 and 0.040-8.110, respectively.

Keywords: Shatt Al-Hilla river, Surface water pollution, Pb, Ni and Fe.

INTRODUCTION

Pollution of surface water and underground water system through anthropogenic activities is the major problem which faced environment for all around the globe. Pollution with heavy metals are widespread of great environmental concern as they are toxic, non degradable and existence with serious ecological ramifications on aquatic ecology[1,2]. Heavy metals are widely used in pesticides, house-holds appliances, mining industries, dental amalgams, photographic papers, paints, photo chemicals, automobiles, *etc.*[3,4]. Several techniques have been used to determine heavy metals in environmental samples. This techniques include flame and graphite furnace atomic absorption spectrometry[5], inductively coupled plasma mass spectrometry (ICP-MS)[6-13], neutron activation analysis[14], inductively coupled plasma optical emission spectrometry (ICP-OES)[15-22], electro thermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS)[23], flow injection sold phase extraction inductively coupled plasma mass spectrometry (FI-SPE-ICPMS)[24], inductively coupled plasma emission spectrometry (ICP-ES)[25] and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)[26]. Heavy metals are link to several human diseases. For instance, Pb affects young children, primarily decreasing neurobehavioral and neurons psychological outcomes in growing children[27,28]. The rank of Pb is the second in top twenty lists of the most poisoning heavy metals (after arsenic), its target organs are the bones, blood, kidneys, reproductive and cardiovascular systems, brain and thyroid gland[29,30]. The main target organs for Cd are the kidneys and liver[31,32]. Exposure to high levels of Zn may cause muscle pain, acute renal failure, pancreatitis, anemia and death. The main target organs of Feare the kidneys, cardiovascular system and liver[33]. Certain human illness is related to Cr consumption such as allergic skin reaction, chronic ulceration and perforation of the nasal septum[34]. Over exposure to Ni cancause heart and liver damage, decreased body weight and skin irritation[27]. Therefore monitoring these metals is very important for safety assessment of the environment and human health especially.

In Iraq and particularly in Al-Hilla city, urban agriculture has been a normal practice along both river banks. Previous studies were reported that the pollution existed by toxic chemicals and heavy metals from industries which discharge waste water untreated into river stream directly, discharge of effluents from domestic and municipal sewage, agricultural activation, oil and lubricant and car washing. For these reasons, this work objective to monitor the river water over long period of time in order to describe average metal contamination and its trend, which is essential component of any pollution control management.

EXPERIMENTAL

Description of study area: The Shatt Al-Hilla river is one of the most important rivers for water supply and irrigation in the Babylon Governorate. The total length of this river is 97 km. Many pollution sources are present near this river such as draining sewage, agriculture pumps and textile factories treated wastewater. The Shatt AL-Hilla river starts from Saddat Al-Hindya and finishes on the southern borders of Al-Hilla city in Sadder Al-Dughara, passing through several villages and cities. These sites were selected during a boat trip to explore the sites contaminated. Study area was described in previous work[35].

Sampling and collection of water samples: A total of 168 water samples were collected along Shatt Al-Hilla from fourteen sampling point between Novembr-2011 and October-2012. Water samples were collected from a depth of 1ft below the surface using polyethylene containers 1 L. The containers are washed well with detergent then with distilled water and soaked in 10 % nitric acid then washed water sample twice and finally filled with the water sample and 2 mL of concentrated HNO_3 is added and the container is capped sealed and sent to the laboratory where the sample is filtered by passing through 0.45 μm membrane filter[36].

Analytical methods: The heavy metals were analyzed by using GBC scientific equipment flame atomic absorption spectrophotometer by applying the following parameters in triplicate analysis: Table-1, illustrate the parameters were applied for all samples. All chemicals were used for preparation of standard solution for the calibration curve is of analar grade chemicals. 150 mL of sample was transferred to a beaker (250 mL), 5 mL of concentrated nitric acid was added and the mixture evaporated to dryness on a hot plate. (1-2) mL of concentrated nitric acid was added to dissolve all the residues on the walls of the beaker. The distilled, digested samples were filtered and made more than 50 mL and analyzed by atomic absorption spectrometer (AAS). The blank was prepared by carrying distilled deionized water for all the above procedure[37,38].

TABLE-1
OPERATING PARAMETERS OF ATOMIC ABSORPTION ANALYSIS

Metal	Wavelength (HCl) (nm)	Slit width (nm)	HCL current (mA)	Flame composition
Pb	217.0	0.2	5	Air-Acetylene flame
Ni	232.0	0.2	4	Air-Acetylene flame
Fe	248.3	0.2	5	Air-Acetylene flame

RESULTS AND DISCUSSION

The results of the determination are presented in Tables 2-4, respectively. These tables show concentrations of lead, nickel and iron in water samples from various sampling location during 12 months. Variation in the heavy metals concentration results due to the site position and the month of sampling which is summarized as follows: The concentration of lead varied from 0.03 ppm as lowest result recorded on sites 1, 2, 8 and 11 in August 2012 while the maximum concentration was 16.6 ppm recorded on site 14 in November 2011. The mean value of Pb concentration for all the sites shows a maximum value of 8.976 ppm in November 2011 and a minimum of 0.21 ppm in July 2012. The results are shown in Table-2. The mean concentration of lead in water was found extremely higher than the permissible limit for lead in drinking water which is less than 0.05 ppm according to WHO[39]. The highest concentration of lead may be attributing to the accumulation effect for the previous sites which they locate before this site, by moving with water stream to be at highest value in this location especially if we take in consideration that is in this location no pollution source. The factories which located in study area such as Al-Sadda cement factory and Al-Furat establishment for chemical production may be contribute to elevate the heavy metals levels generally and lead specially in study area. Standards which is very dangerous as lead poising causes gastrointestinal, neuromuscular and central nervous system disorders and also cause liver and kidney damage, reduced hemoglobin formation and infertility and birth defects.

TABLE-2
CONCENTRATIONS OF LEAD FOR ONE YEAR DISTRIBUTED ON FOURTEEN SITES

	Pb (ppm)												Range (ppm)	
Site No.	Nov. 2011	Dec. 2011	Jan. 2012	Feb. 2012	Mar. 2012	Apr. 2012	May. 2012	Jun. 2012	Jul. 2012	Aug. 2012	Sep. 2012	Oct. 2012	Min	Max
S_1	1.800	1.630	14.500	2.340	1.280	0.400	0.280	0.200	0.130	0.030	0.086	0.400	0.030	14.500
S_2	6.000	1.540	8.000	2.800	1.280	0.300	0.350	0.800	0.060	0.030	0.073	1.200	0.030	8.000
S_3	0.200	1.450	11.000	1.980	0.700	0.400	0.350	0.400	0.260	0.800	0.800	0.800	0.200	11.000
S_4	13.100	1.800	3.250	2.440	2.280	0.500	0.210	0.900	0.400	0.500	0.930	0.730	0.210	13.100
S_5	2.450	2.000	13.750	3.400	2.600	0.400	0.350	0.700	0.460	0.300	0.860	0.600	0.300	13.750
S_6	4.560	1.630	11.250	2.030	1.000	0.500	0.210	0.800	0.260	0.400	1.060	0.330	0.210	11.250
S_7	7.200	2.000	2.250	2.230	4.700	0.700	0.350	0.100	0.060	0.500	0.800	1.100	0.100	7.200
S_8	8.860	1.800	2.250	3.250	1.700	0.500	0.070	0.600	0.060	0.030	1.060	0.730	0.030	8.860
S_9	11.040	1.900	5.500	3.570	2.780	0.700	0.280	0.400	0.260	0.200	0.860	0.660	0.200	11.040
S_{10}	9.060	1.000	5.750	1.980	0.420	0.800	0.350	0.800	0.730	0.300	1.060	0.730	0.300	9.060
S_{11}	13.700	0.720	11.250	2.750	1.320	0.800	0.280	0.700	0.060	0.030	0.860	0.930	0.030	13.700
S_{12}	16.0900	0.900	8.750	2.400	4.500	1.000	0.210	0.500	0.080	0.100	0.930	0.130	0.080	16.090
S_{13}	15.000	1.180	9.500	2.000	2.000	1.000	0.350	0.400	0.060	0.500	1.260	0.600	0.060	15.000
S_{14}	16.600	1.450	10.000	1.400	1.280	0.900	0.350	0.060	0.060	0.100	1.060	0.600	0.060	16.600
Mean	8.975	1.500	8.357	2.469	1.988	0.635	0.285	0.525	0.210	0.272	0.835	0.681	0.131	12.082

The high concentration of lead in the river can be related to the discharge in the surface water through paints, solders, pipes, building materials and combustion of oil and gasoline which accounts for more than 50 % of all anthropogenic emmitions and the atmospheric fallout is usually the most important source of lead in fresh water[40].

The minimum concentration of Ni in water recorded was 0.08 ppm at site 7 in January 2012 and 4 in March 2012 and the maximum value 10.6 ppm was recorded at site 13 in April 2012. Whereas the mean value of Ni concentration in water for all sites showed a maximum value of 5.19 ppm in January 2012 and the minimum value of 0.168 ppm in February 2012. The results are shown in Table-3. The presence of high concentration of nickel in Shatt Al-Hilla river is observed as the mean concentration is greater than the permitted limit which is 0.02 ppm and this causes nickel toxicity with the symptoms of skin rash, giddiness, diarrhea and also can lead to swelling of brain and liver, degeneration of liver, irritation to the eyes, throat and nose and various types of cancer. The nickel toxicity sources are hydrogenated oils, electroplating, industries dealing with electrical equipment and house hold appliances, catalysts, pigments, batteries Ni-Cd and coal and oil combustion are the major source of nickel concentration in the water bodies. The maximum value of nickel was recorded in site thirteen, the pollution source for this site is existence of filtration station for drinking water and this station is use the pipe out let from the precipitating tanks to remove all the sediments and precipitants which remove from these tanks to river. Heavy metals in nature tend to be down in these tank, therefore when the precipitants are removed they going in high percentage at the removing time.

Iron concentrations were found to be high at certain sites in one month and differs greatly in other time also there is differences between the different sites values. The maximum value of Fe concentration gained was 8.11 ppm at site 10 in Faberuary 2012 while the minimum value was 0.004 ppm at sites 1 and 14 in December 2011. The mean value of Fe concentration for all the sites shows a maximum value of 6.044 ppm in Fabruary 2012 and a minimum of 0.09 ppm in December 2011. The results are shown in Table-4. The observed experimental value of iron mean concentration in water was very much higher than the permissible limit of iron which 0.3 ppm when the presence of high concentration of Iron may increase the hazards of pathogenic organisms since they need Iron for their growth[40] and also causes nausea, vomiting, brain hemorrhage, anxiety, tension, cardiac arrest and metabolic disorder. The higher concentration levels of iron may be it is seeped through contaminated soil and entered the river along with

TABLE-3
CONCENTRATIONS OF NICKEL FOR ONE YEAR DISTRIBUTED ON FOURTEEN SITES

	Ni (ppm)												Range (ppm)	
Site No.	Nov. 2011	Dec. 2011	Jan. 2012	Feb. 2012	Mar. 2012	Apr. 2012	May. 2012	Jun. 2012	Jul. 2012	Aug. 2012	Sep. 2012	Oct. 2012	Min	Max
S_1	1.110	6.290	0.240	0.360	0.100	0.300	0.350	3.700	5.200	5.750	3.500	0.230	0.100	6.290
S_2	0.920	2.800	0.200	0.460	0.100	0.430	0.460	3.600	4.560	5.000	4.300	0.230	0.100	5.000
S_3	0.100	2.900	0.120	0.160	0.700	0.150	0.200	2.800	3.470	3.750	3.300	0.200	0.100	3.750
S_4	1.560	3.400	0.080	0.400	0.190	0.430	0.390	4.200	4.820	5.400	5.000	0.260	0.080	5.400
S_5	1.300	3.700	0.200	0.300	0.220	0.320	0.350	2.500	3.210	3.450	2.300	0.160	0.160	3.700
S_6	1.000	3.800	0.200	0.230	6.900	0.230	0.250	3.800	3.820	4.500	4.300	0.160	0.160	6.900
S_7	1.000	3.890	0.080	0.400	2.800	0.400	0.280	3.300	3.780	4.100	3.800	0.230	0.080	3.890
S_8	1.470	4.700	0.200	0.300	0.100	0.300	0.300	3.000	3.260	3.900	3.300	0.230	0.100	4.700
S_9	1.170	6.300	0.200	0.460	6.470	0.440	0.400	2.900	3.390	3.500	3.300	0.230	0.200	6.470
S_{10}	1.070	6.500	0.200	0.430	0.100	0.400	0.450	4.600	7.130	7.950	5.000	0.160	0.100	7.950
S_{11}	1.760	6.500	0.120	0.200	6.600	0.200	0.190	2.600	3.000	3.250	2.800	0.160	0.120	6.600
S_{12}	1.170	6.800	0.200	0.360	4.800	0.300	0.320	3.300	3.820	4.250	3.800	0.160	0.160	6.800
S_{13}	1.000	7.300	0.200	0.160	10.600	0.200	0.200	3.500	4.000	4.500	4.200	0.160	0.160	10.600
S_{14}	1.210	7.800	0.120	0.500	13.000	0.530	0.550	2.000	2.520	2.750	2.300	0.160	0.120	13.000
Mean	1.131	5.191	0.168	0.337	3.762	0.330	0.335	3.271	3.998	4.432	3.657	0.195	0.124	6.503

TABLE-4
CONCENTRATIONS OF IRON FOR ONE YEAR DISTRIBUTED ON FOURTEEN SITES

	Fe (ppm)												Range (ppm)	
Site No.	Nov. 2011	Dec. 2011	Jan. 2012	Feb. 2012	Mar. 2012	Apr. 2012	May. 2012	Jun. 2012	Jul. 2012	Aug. 2012	Sep. 2012	Oct. 2012	Min	Max
S_1	0.310	0.004	0.200	6.600	1.500	0.250	0.260	0.200	0.200	0.200	0.200	0.200	0.004	6.600
S_2	0.130	0.013	0.187	6.300	0.050	0.150	0.170	0.200	0.200	0.200	0.200	0.200	0.013	6.300
S_3	0.200	0.008	0.200	7.460	2.300	0.100	0.150	0.200	0.200	0.200	0.200	0.200	0.008	7.460
S_4	0.310	0.009	0.200	6.000	0.530	0.150	0.100	0.200	0.200	0.200	0.200	0.200	0.009	6.000
S_5	0.220	0.200	0.200	5.460	0.050	0.300	0.320	0.200	0.050	0.200	0.200	0.200	0.050	5.460
S_6	0.310	0.200	0.200	7.110	0.480	0.500	0.500	0.200	0.200	0.200	0.200	0.200	0.200	7.110
S_7	0.220	0.200	0.125	6.460	0.050	0.350	0.370	0.200	0.083	0.200	0.200	0.200	0.050	6.460
S_8	0.130	0.200	0.187	5.690	0.050	0.150	0.180	0.200	0.200	0.200	0.200	0.200	0.050	5.690
S_9	0.220	0.008	0.187	4.400	0.050	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.008	4.400
S_{10}	0.310	0.008	0.187	8.110	0.050	0.100	0.130	0.200	0.200	0.200	0.200	0.200	0.008	8.110
S_{11}	0.220	0.200	0.25 0	4.950	0.050	0.250	0.250	0.200	0.200	0.200	0.200	0.200	0.050	4.950
S_{12}	0.310	0.200	0.125	5.460	0.050	0.400	0.400	0.200	0.200	0.200	0.200	0.200	0.050	5.460
S_{13}	0.170	0.008	0.187	4.730	2.280	0.300	0.280	0.200	0.200	0.200	0.200	0.200	0.008	4.730
S_{14}	0.220	0.004	0.312	5.880	0.050	0.400	0.500	0.200	0.200	0.200	0.200	0.200	0.004	5.880
Mean	0.234	0.090	0.192	6.043	0.538	0.257	0.272	0.200	0.180	0.200	0.200	0.200	0.036	6.043

the rain water run-off. The maximum value of iron was in site ten, in this site which the boats are spread using different types of fuels for their engines. The main product for iron oxide is that the flout bodies made of iron as a result of corrosion and also that produce from these engine which contribute to raise the iron levels in this site.

Conclusion

In conclusion Pb, Ni and Fe have shown elevated levels of heavy metals at many sites along Shatt Al-Hilla river in different seasons of the study. The increased levels of heavy metals in the water lead to accumulation of them in the agricultural soils and plants grown on the contaminated soils leading to great harm to humans and animals. Hence, it is obligatory to rectify the various heavy metals resources which lead to addition of these metals into the river. Also, water should be tested systematically and regularly to keep monitoring process on the heavy metals pollutant into the water and purify the water, if necessary. Further, as the heavy metals enter the food chain and get accumulated at each level from producers to consumers the heavy metal concentrations in soil and in various crops grown in the area is to be examined in addition to the river sediments which affected the aquatic life in the river.

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