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Spatial and Monthly Variation in Co, Zn and Cd Concentrations of Surface Water of Shatt Al-Hilla River, Babylon, Iraq

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This study was focused on the spatial and monthly variation in the concentration of Co, Zn and Cd in surface water of Shatt Al-Hilla river. Fourteen sampling sites have been selected of pollution located on the both banks of Shatt Al-Hilla river. Samples were analyzed by flame atomic absorption spectrometry. Several physico-chemical properties of water samples were measured during period of study such as pH values, electric conductivity and temperature of water. Study was started from November 2011 and finished in October 2012. The concentrations of heavy metals under concern exhibit wide variation from site to site and from month to month. The pH values were ranged between 6.4 to 8.9, while electric conductivities were ranged between 819 to 1250 μS. The concentrations of Co and Zn were ranged 0.012 to 5.400 and 0.10 to 2.30 mg/L, respectively whereas Cd was detected in 0.007-1.550 mg/L range.

Keywords: Shatt Al-Hilla river, Surface water pollution, Co^{2+}, Zn^{2+} and Cd^{2+}.

INTRODUCTION

The contamination of water resources by heavy metals is a serious problem that can affect the environment since some of the heavy metals are very harmful[1]. Heavy metals are among the most persistent of contaminants in the ecosystem such as biota, sediments and water, because of their resistance to decompose in natural condition. Toxicity appears after increasing the level of indispensability. Heavy metals become toxic when they are be not metabolize by the human body and accumulate in the soft tissues of this body[2]. Generally, in uninfected environment, most of the heavy metals are in very low levels and natural geological weathering of soil and rocks, directly exposed to surface waters, is usually the largest natural source. Main pollution with heavy metals by anthropogenic sources are mining, disposal of partially treated and untreated effluents contain toxic metals, as well as metal chelates from several industrial factories and indiscriminate use of fertilizer containing heavy metals. Heavy metals discharged into aquatic system by anthropogenic sources or natural during their transport are distributed between two phases: aqueous and sediments. Because of the following processes such as adsorption, hydrolysis and co-precipitation only a small portion of free metal ions stay dissolved in water while a large quantity of the metals deposited in the sediment. Although heavy metals are refractory though natural processes in the environment, they can be chemically changed by microorganisms and convert to organic complexes, some of which may be more hazardous to aquatic animals and human life[3]. Potentially toxic heavy metals, including zinc, cadmium and others, may participate in reactions and accumulate, causing deleterious effects in aquatic organisms[4]. The maximum allowed concentrations in drinking water of heavy metals are in the ppb range (*e.g.*, 5 ppb for Cd and 110 ppb for Co)[5]. There are over 50 heavy metals that can be classified as heavy metals, only 17 of which are considered to be very toxic and relatively accessible[1]. The heavy metals in drinking water linked most often to human poisoning are copper, cadmium, zinc, *etc*. They are required by the body in small concentrations, but can also be toxic in large amounts. Cadmium is extremely toxic metal even in low amounts, it has a long biological half-life in the human body and the half-life of cadmium is range from 10 to 33 years. Long term exposures to this element also induce renal damage[6].

Recently several techniques were used to determine heavy metals in environmental samples. These techniques include inductively coupled plasma mass spectrometry (ICP-MS)[7-14]; flame and graphite furnace atomic absorption spectrometry[15]; inductively coupled plasma optical emission spectrometry (ICP-OES)[16-23]; neutron activation analysis[24], electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS)[25]; inductively coupled plasma emission spectrometry (ICP-ES)[26]; flow injection solid phase extraction inductively coupled plasma mass spectrometry (FI-SPE-

ICPMS)[27] and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)[28]. In Iraq and particularly in study area (Al-Hilla city), urban agriculture has been a normal practice along both river banks. The objective of this work is monitoring the rivers water over a long period of time in order to describe average metal pollution and its trend, which is essential component of any pollution control management.

EXPERIMENTAL

Description of study area: Shatt Al-Hilla river is one of the main sources of water in the Babylon Governorate. This river starts from Saddat Al-Hindya and finishes on the southern borders of Al-Hilla city. Study area was described in previous work[29].

Sampling, collection of water samples and analytical methods: Water samples have been collected from fourteen sites once monthly during the study period started in November 2011 and finished in October 2012. Sampling method was mentioned in previous work[30]. The operating parameters of the atomic absorption analysis are given in Table-1.

TABLE-1
OPERATING PARAMETERS OF THE ATOMIC ABSORPTION ANALYSIS

Metal	Wavelength (HCL) (nm)	Slit width (nm)	HCL current (mA)	Flame composition
Co	240.7	0.2	6	Air-acetylene flame
Zn	213.9	0.2	5	Air-acetylene flame
Cd	228.8	0.2	3	Air-acetylene flame

RESULTS AND DISCUSSION

The results of the determination are presented in Tables 2-4. These Tables show concentrations of Co^{2+}, Zn^{2+} and Cd^{2+} ions in water samples from various sampling locations during twelve months. Variation in the heavy metals concentration results due to the site position and the month of sampling which summarized as: The minimum value of cobalt concentration 0.012 ppm was recorded at sites 7, 8, 11 and 12 in October 2012 and the maximum value 5.4 ppm was recorded at site 3

TABLE-2
CONCENTRATIONS OF COBALT FOR FOURTEEN SITES DURING TWELVE MONTHS

	Co (ppm)												Range (ppm)	
Site Number	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	1.600	0.080	0.750	0.100	1.700	0.700	0.100	0.200	0.160	0.120	0.160	0.120	0.080	1.700
S_2	0.800	0.120	0.500	0.100	5.200	0.100	0.100	0.130	0.126	0.160	0.160	0.120	0.100	5.200
S_3	0.100	0.120	0.500	0.100	5.400	0.100	0.100	0.160	0.160	0.120	0.130	0.160	0.100	5.400
S_4	1.000	0.160	1.000	0.100	0.690	1.000	0.100	0.130	0.080	0.120	0.130	0.120	0.100	1.000
S_5	2.000	0.120	0.250	0.100	2.700	0.100	0.100	0.130	0.126	0.160	0.130	0.080	0.080	2.700
S_6	2.800	0.160	0.500	0.100	2.600	0.100	0.100	0.200	0.200	0.160	0.200	0.080	0.080	2.800
S_7	2.000	0.200	0.500	0.100	1.700	0.100	0.100	0.160	0.160	0.160	0.160	0.012	0.012	2.000
S_8	1.000	0.080	0.500	0.100	1.900	0.100	0.100	0.080	0.080	0.120	0.130	0.012	0.012	1.900
S_9	1.600	0.080	0.500	0.100	1.400	0.100	0.100	0.130	0.126	0.120	0.130	0.080	0.080	1.600
S_{10}	2.000	0.120	0.500	0.100	3.000	0.200	0.100	0.160	0.160	0.160	0.160	0.080	0.100	3.000
S_{11}	2.400	0.160	0.500	0.100	1.900	0.100	0.100	0.080	0.080	0.080	0.130	0.012	0.012	2.400
S_{12}	1.800	0.120	0.500	0.100	3.600	0.100	0.200	0.080	0.126	0.120	0.130	0.012	0.012	3.600
S_{13}	0.400	0.080	0.500	0.100	2.600	0.100	0.100	0.160	0.200	0.160	0.160	0.080	0.080	2.600
S_{14}	3.000	0.080	1.000	0.100	4.400	0.300	0.100	0.080	0.160	0.120	0.130	0.080	0.080	4.400
Mean	1.607	0.120	0.571	0.100	2.770	0.228	0.107	0.134	0.138	0.134	0.145	0.074	0.066	2.878

TABLE-3
CONCENTRATIONS OF ZINC FOR FOURTEEN SITES DURING TWELVE MONTHS

	Zinc (ppm)												Range (ppm)	
Site Number	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	2.000	0.060	0.030	0.730	0.017	0.032	0.056	0.250	0.260	0.240	0.220	0.024	0.017	2.000
S_2	1.700	0.220	0.100	0.660	0.017	0.032	0.024	0.050	0.060	0.110	0.030	0.032	0.017	1.700
S_3	0.030	0.140	0.100	0.730	0.036	0.024	0.048	0.120	0.140	0.110	0.010	0.024	0.010	0.730
S_4	1.710	0.190	0.100	0.670	0.036	0.040	0.032	0.170	0.190	0.130	0.140	0.032	0.032	1.710
S_5	1.480	0.260	0.030	0.560	0.078	0.024	0.024	0.070	0.080	0.080	0.070	0.024	0.024	1.480
S_6	1.210	0.110	0.100	1.250	0.069	0.040	0.032	0.050	0.039	0.300	0.050	0.024	0.024	1.250
S_7	1.890	0.080	0.100	1.440	0.095	0.032	0.032	0.110	0.100	0.080	0.130	0.024	0.024	1.890
S_8	1.700	0.039	0.100	0.670	0.069	0.024	0.024	0.180	0.190	0.150	0.160	0.032	0.024	1.700
S_9	1.950	0.070	0.100	0.760	0.036	0.032	0.040	0.170	0.140	0.100	0.140	0.024	0.024	1.950
S_{10}	2.730	0.100	0.030	1.000	0.078	0.040	0.032	0.060	0.060	0.080	0.050	0.024	0.024	2.730
S_{11}	2.070	0.050	0.020	0.700	0.060	0.024	0.032	0.210	0.030	0.200	0.210	0.032	0.020	2.070
S_{12}	1.360	0.060	0.100	0.610	0.052	0.040	0.046	0.120	0.100	0.110	0.110	0.032	0.032	1.360
S_{13}	1.870	0.098	0.020	0.440	0.036	0.060	0.064	0.050	0.390	0.040	0.060	0.024	0.020	1.870
S_{14}	1.270	0.058	0.100	0.780	0.043	0.032	0.056	0.070	0.080	0.090	0.070	0.024	0.024	1.270
Mean	1.640	0.109	0.073	0.785	0.051	0.034	0.038	0.120	0.132	0.130	0.103	0.026	0.022	1.693

in March 2012. The mean value of Co concentration in water for the all sites shows a maximum value of 2.628 ppm in March 2012 and the minimum value of 0.066 ppm in October 2012. The results are shown in Table-2. The higher contents of cobalt in water is dangerous[31] as it is carcinogenic and the low concentration of it causes vomiting, weakness, lack of concentration, hearing impairment, thyroid problems and cardio vascular disease. Cobalt enters the water from the effluents of industries dealing with corrosion and wear resistant alloys, colors, pigments and petroleum based industries. Previous studies indicate that the major sources of cobalt are domestic and industrial effluents[32,33]. The maximum value of zinc concen-tration in water samples obtained was 1.98 ppm at site 13 in November 2011 and the minimum value was 0.01 ppm at site 3 in September 2012. The mean value of Zn concentration for all sites showed a minimum value of 0.027 ppm in October 2012 and the maximum of 1.641 ppm in November 2011. The results are presented in Table-3. The concentration of zinc observed is in the range permitted by the global regulations. Zinc is involved in various physiological and metabolic activities of many organisms but increase level of it can made many health disorder[34]. The sources of Zn into the water bodies could be effluents of electroplating, sewage effluents. The concentrations of zinc were in the range of WHO and EU.

The cadmium concentration is varied from 0.002 ppm as a minimum value recorded at site 4 in May 2012 to the maximum value of 1.55 ppm at site 12 in December 2011. The mean value of Cd concentration in water for all sites shown a maximum value of 1.372 ppm in December 2011 and the minimum value of 0.024 ppm in September 2012. The results are presented in Table-4. The higher concentration of cadmium than limits which is 0.003 ppm is very dangerous as cadmium is poisonous metal and can cause serious health problems and it has the tendency to accumulate in the body tissues that results in lung problems and kidney damage[35]. Effluents from battery industries, dyes, pigments and alloy making are the major sources of cadmium in the water. The conductivity values (Table-6) for surface water ranged 822-1250 are within the safe limit of application.

The mean pH values in Table-5 for surface water ranged between 7.815 to 8.644, increasing in the range of pH value start from the upstream to downstream of the river which refer to increase the alkalinity in down direction of the river. The observed pH of the river water was well within the safe limit values for drinking and EU as well as for crop production. The

TABLE-4
CONCENTRATIONS OF CADMIUM FOR FOURTEEN SITES DURING TWELVE MONTHS

	Cd (ppm)												Range (ppm)	
Site Number	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	0.550	1.350	0.220	0.060	0.100	1.000	0.018	0.050	0.040	0.050	0.016	0.060	0.016	1.350
S_2	0.065	1.300	0.220	0.180	0.100	0.400	0.070	0.050	0.040	0.050	0.016	0.120	0.016	1.300
S_3	0.100	1.400	0.220	0.250	0.040	0.800	0.019	0.050	0.033	0.050	0.008	0.160	0.019	1.400
S_4	0.260	1.340	0.034	0.250	0.016	0.900	0.002	0.050	0.040	0.050	0.016	0.120	0.002	1.340
S_5	0.290	1.440	0.022	0.130	0.100	1.000	0.035	0.050	0.050	0.050	0.033	0.080	0.022	1.440
S_6	0.350	1.460	0.056	0.150	0.076	0.800	0.007	0.050	0.050	0.050	0.025	0.080	0.007	1.460
S_7	0.390	1.500	0.022	0.170	0.100	1.000	0.041	0.050	0.040	0.050	0.025	0.012	0.012	1.500
S_8	0.350	1.400	0.022	0.180	0.100	1.000	0.032	0.050	0.059	0.050	0.025	0.012	0.012	1.400
S_9	0.420	1.420	0.022	0.170	0.016	0.900	0.041	0.050	0.040	0.050	0.033	0.080	0.016	1.420
S_{10}	0.420	1.500	0.056	0.140	0.100	1.200	0.031	0.050	0.016	0.050	0.033	0.080	0.016	1.500
S_{11}	0.450	1.380	0.079	0.200	0.016	1.000	0.053	0.050	0.059	0.050	0.033	0.012	0.012	1.380
S_{12}	0.480	1.550	0.022	0.180	0.016	1.000	0.044	0.050	0.040	0.050	0.033	0.012	0.012	1.550
S_{13}	0.420	0.650	0.068	0.200	0.040	0.900	0.042	0.050	0.040	0.050	0.025	0.080	0.025	0.900
S_{14}	0.420	1.520	0.100	0.210	0.016	1.200	0.064	0.050	0.033	0.050	0.016	0.080	0.016	1.520
Mean	0.354	1.372	0.083	0.176	0.059	0.935	0.035	0.050	0.041	0.050	0.024	0.070	0.014	1.390

TABLE-5
pH VALUES FOR FOURTEEN SITES DURING TWELVE MONTHS (YEAR 2011-2012)

Site no.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Max.	Min.
S1	6.4000	6.810	6.880	6.700	6.700	6.780	6.900	8.320	8.330	8.350	7.660	8.280	8.35	6.4
S2	6.600	6.530	6.590	7.070	7.070	7.150	7.650	8.350	8.350	8.370	7.760	8.450	8.45	6.53
S3	6.600	6.370	7.060	7.220	7.220	7.840	8.040	8.430	8.450	8.470	8.190	8.470	8.47	6.37
S4	6.600	6.570	6.730	7.110	7.110	7.180	7.970	8.430	8.430	8.460	8.200	8.520	8.52	6.57
S5	6.800	6.420	6.980	7.000	7.000	7.200	8.240	8.200	8.250	8.320	8.100	8.490	8.49	6.42
S6	6.800	6.630	6.710	7.280	7.280	7.380	8.304	8.550	8.600	8.630	8.490	8.750	8.75	6.63
S7	7.000	6.600	6.660	7.610	7.610	7.650	8.440	8.500	8.480	8.510	8.580	8.770	8.77	6.6
S8	7.100	6.960	6.960	7.090	7.090	8.090	8.760	8.510	8.500	8.530	8.360	8.760	8.76	6.96
S9	7.200	6.560	6.560	7.600	7.600	7.660	8.900	8.520	8.570	8.590	8.200	8.800	8.9	6.56
S10	7.300	6.910	6.910	7.700	7.700	7.701	8.740	8.570	8.560	8.590	8.490	8.790	8.79	6.91
S11	7.400	6.900	7.110	7.830	7.830	7.840	8.840	8.640	8.650	8.660	8.640	8.930	8.93	6.9
S12	7.400	6.870	7.080	7.910	7.91	7.960	8.560	8.590	8.500	8.530	8.410	8.690	8.69	6.87
S13	7.500	6.990	7.230	7.920	7.920	8.510	8.560	8.500	8.470	8.480	8.440	8.630	8.63	6.99
S14	7.600	7.080	7.240	7.880	7.880	8.340	8.340	8.440	8.350	8.350	8.200	8.520	8.52	7.08
Mean	7.021	6.728	6.907	7.422	7.422	7.663	8.305	8.467	8.463	8.488	8.265	8.632	8.644	6.699

TABLE-6
CONDUCTIVITY VALUES FOR FOURTEEN SITES DURING TWELVE MONTHS (YEAR 2011-2012)

Site no.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Max.	Min.
S1	867	870	880	983	978	1022	1060	844	1068	1071	1020	1000	1071	844
S2	889	881	885	978	991	1038	1068	847	1096	1095	1083	1086	1096	847
S3	963	932	930	1061	1070	1068	1067	849	1099	1098	1014	1017	1099	849
S4	844	848	876	999	1010	998	1064	863	1074	1079	1018	1013	1079	844
S5	914	897	904	1041	1033	1047	1077	836	1088	1090	1000	1020	1090	836
S6	995	1002	993	1040	1038	1038	1075	1005	1051	1056	1006	1013	1075	993
S7	877	872	870	1011	1019	1040	1076	1250	1170	1169	1189	1013	1250	870
S8	862	856	855	1021	1020	1042	1076	864	1142	1153	1186	1021	1186	855
S9	860	859	866	1059	1044	1055	1063	930	1094	1090	1041	1018	1094	859
S10	835	840	886	1054	1053	1049	1127	870	1092	1089	1042	1007	1127	835
S11	910	921	920	1076	1057	1077	1072	860	1076	1081	1069	1007	1081	860
S12	822	819	839	1081	1072	1073	1080	852	1074	1068	999	1010	1081	819
S13	907	893	890	1078	1070	1082	1085	848	1074	1080	1008	1015	1085	848
S14	844	837	841	1047	1055	1021	1093	836	1078	1077	1009	1045	1093	836
Mean	884	880	888	1037	1036	1046	1077	896	1091	1092	1048	1020	1107	856

conductivity values (Table-6) for surface water ranged 822-1250 are within the safe limit of application.

Conclusion

In conclusion, Co, Zn and Cd 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 levels 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 will affect the aquatic life in the river.

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