World Applied Sciences Journal 6 (9): 1209-1214, 2009
ISSN 1818-4952

Determination of Heavy Metals in Zayandeh Rood River, Isfahan-Iran

[1]Y. Sanayei, [1]Norli Ismail and [2]S.M. Talebi

[1]School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Pinang, Malaysia
[2]Department of Chemistry, Isfahan University, P.O. Box 81745-137, Isfahan 81744, Iran

Abstract: Zayandeh-Rood is one of the most important rivers flows in the central Part of Iran. The river source is located in Koohrang Mountains. The river passes through two Provinces; Chaharmohal-Bakhtiari and Isfahan. The river at the end discharges to the Gavkhooni Wetland. The river water is used for drinking, industrial and agricultural purposes. The determination of pollutants such as pesticides, heavy metals and other chemical parameters through out the river is important and has a great role in the control of the ecological condition of this water media. The anthropogenic impact on the environment in the last four decade has proven to be extremely negative due to the quick development of industry. An example is the Zayandeh Rood River in center of Iran, one of the most polluted sites in this region. Trace elements concentrations (Cd, Cu, Mn, Ni, Pb and Zn) were measured seasonal in the Zayandeh Rood River waters during October 2004 to September 2005. In the present work, ICP-AES as a multi-elemental technique has been used for the determination of trace heavy metals. No Significant differences between the seven studied sites were observed for heavy metals and this result was attributed to the influence of the industrial activities in the region and/or the municipal runoff in this area.

Key words: Heavy metals % Trace elements % Zayandeh Rood

INTRODUCTION

Heavy metals pollution represents a serious problem for human health and for life in general. The disposal of heavy metals is a consequence of several activities like chemical manufacturing, painting and coating, mining, extractive metallurgy, nuclear and other industries. Those metals exert a deleterious effect on fauna and flora of lakes and streams [1]. Human activities such as industrial and municipal effluents, as well as atmospheric deposition and non-point source run-off have are the main sources of metals in rivers. They are one the most environmental pollutant which accumulates in living organisms. Its cumulative poisoning effects are serious hematological and brain damage, anemia and kidney malfunctioning [2]. Heavy metals in different river are most investigated recently [3-5]. The toxicity of heavy metals has long been concerned since it is very important to the health of people and ecology. Heavy metals can also accumulate in the soil at toxic levels as a result of long-term application of untreated wastewaters. Soils irrigated by wastewater accumulate heavy metals such as Cr, Zn, Pb, Cd, Ni, etc in surface soil. When the capacity of the soil to retain heavy metals is reduced due to repeated application of wastewater, heavy metals leach into ground water or soil solution available for plant uptake [6]. Among different techniques, flame atomic absorption spectrometry (FAAS) is the most frequently used and the popular one. FAAS technique is classified as a single-elemental method and requires long time for analysis of several elements in a sample. In air pollution studies, several metals have to be determined in a huge number of samples and in a short period of time. FAAS is time-consuming and tedious. Multi-elemental techniques such as x-ray fluorescence (XRF) [7], neutron activation analysis (NAA) [8, 9] and inductively coupled plasma atomic emission spectrometry (ICP-AES) [10, 11] have been exported for simultaneous determination of heavy metals in environmental samples. Among different techniques, ICP-AES is the most popular technique for simultaneous and sensitive determination of heavy metals and offers reliable results. In the present work, ICP-AES as a multi-elemental technique has been used for the determination of trace heavy metals in water.

Corresponding Author: Y. Sanayei, School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Pinang, Malaysia

Present study reports the analysis of selected metals (Cd, Cu, Mn, Ni, Pb and Zn) in the Zayandeh Rood River in Isfahan, central part of Iran. The Isfahan province is most key industrial centre in Iran. There are different kinds of industries in this province, including steel (the biggest in the country), power plants, aluminum, wood production plants, electronic and computer as well as refinery and petrochemical complexes. Consequently cupper, manganese and lead may leach into the aquatic ecosystem of Zayandeh rood.

MATERIAL AND METHODS

Water samples were collected from seven stations along Zayandeh Rood, Isfahan-Iran, list and specification of sampling point are listed in Table1. Seasonal samplings were cared out during October 2004 to September 2005. Materials associated with trace metal sampling and analyses were thoroughly acid cleaned before use. Metals digestion was done according to USEPA Method 3010 (acid digestion of extracts for total recoverable or dissolved metal analysis by FLAA or ICP spectroscopy) [12]. All reagents were analytical grade. Suprapur® Hydrochloric, hydrofluoric and nitric acids, (Merck, Darmstadt, Germany) were used for sample digestion and preparation of the standards. Standard solutions for ICP determinations (Sigma-Aldrich, MO, USA) of the elements analyzed were used. Glassware and Teflon® vessels were treated in a solution 10% v/v nitric acid for 24 h and then washed with distilled and deionized water. Digested samples were stored in polyethylene tubes of 15 ml and stored in 4° cool room.

The samples were measured using Varian Spectra AA 220 atomic absorption spectrophotometer and an Inductively Coupled-Atomic Emission Spectrometer (ICP-AES) MAXIM model (Fisons, MA, USA). Samples were analyzed in duplicate and triplicate for Cd, Cu, Ni, Pb and Zn. The analytical quality control performed included daily analysis of standard and replicate analysis of samples and blanks [12-14]. The average recovery from the certified reference materials (CRM) varied from 79% for Ni to 106% for Cu, with a mean for the four metals of 89 %.

Table 1: Specification of sampling point

No	Stations	Location
1	Morgan	South west of Isfahan.
2	Pol kaleh	Between Isfahan and chadegan dam
3	Falavarjan	Near city of Isfahan
4	Pole vahid	City of Isfahan
5	Pole khajou	City of Isfahan
6	Pole chom	7 km from Sade Abshar.
7	Pole Varzaneh	Varzaneh city, 125 km east of Isfahan

RESULT AND DISCUSSION

The result of Mean total concentration (ppm) of heavy metals in Zayandeh Rood in autumn, winter, spring and summer are presented in Tables 2-5 respectively.

Table 2: Mean total concentration (ppm) of heavy metals in autumn

Station	Cd	Cu	Mn	Ni	Pb	Zn
Morgan	ND	0.061	0.031	0.72	0.41	0.05
Pole kaleh	0.16	0.069	0.059	0.74	0.37	0.04
Falavarjan	0.14	0.051	0.052	0.51	0.72	0.04
Pole vahid	0.38	0.077	0.079	0.50	0.46	0.07
Pole khajou	0.25	0.081	0.068	0.46	0.41	0.04
Pole chom	0.24	0.062	0.120	0.81	0.37	0.05
Pole varzaneh	0.10	0.089	0.120	1.02	1.41	0.08

Table 3: Mean total concentration (mg l^{-1}) of heavy metals in winter

Station	Cd	Cu	Mn	Ni	Pb	Zn
Morgan	ND	0.052	0.037	0.57	0.38	0.05
Pole kaleh	0.06	0.057	0.041	0.06	0.38	0.04
Falavarjan	0.13	0.051	0.048	0.56	0.59	0.03
Pole vahid	0.83	0.064	0.069	0.59	0.72	0.07
Pole khajou	0.36	0.074	0.065	0.57	0.62	0.06
Pole chom	0.27	0.069	0.069	0.64	0.42	0.06
Pole varzaneh	0.33	0.070	0.072	0.77	1.08	0.06

Table 4: Mean total concentration (mg l^{-1}) of heavy metals in spring

Station	Cd	Cu	Mn	Ni	Pb	Zn
Morgan	0.09	0.041	0.032	0.46	0.29	0.04
Pole kaleh	0.16	0.042	0.029	0.41	0.31	0.06
Falavarjan	0.08	0.050	0.039	0.51	0.49	0.05
Pole vahid	0.55	0.067	0.051	0.61	0.67	0.08
Pole khajou	0.29	0.065	0.067	0.56	0.71	0.06
Pole chom	0.19	0.069	0.071	0.59	0.51	0.05
Pole varzaneh	0.21	0.064	0.072	0.81	0.08	0.07

Table 5: Mean total concentration (mg l^{-1}) of heavy metals in summer

Station	Cd	Cu	Mn	Ni	Pb	Zn
Morgan	0.18	0.062	0.033	0.69	0.44	ND
Pole kaleh	0.07	0.068	0.052	0.72	0.41	0.03
Falavarjan	0.22	0.078	0.076	0.59	0.48	0.04
Pole vahid	0.93	0.086	0.110	1.09	0.89	0.05
Pole khajou	0.62	0.076	0.081	0.82	0.68	0.05
Pole chom	0.34	0.063	0.041	0.71	0.51	0.04
Pole varzaneh	0.55	0.065	0.046	0.69	0.62	0.04

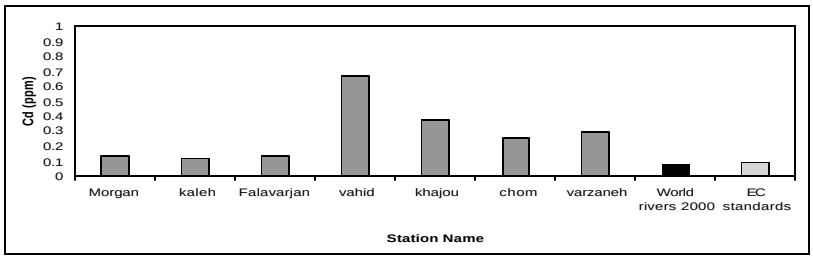

Fig. 1: Average concentration of Cd in different stations

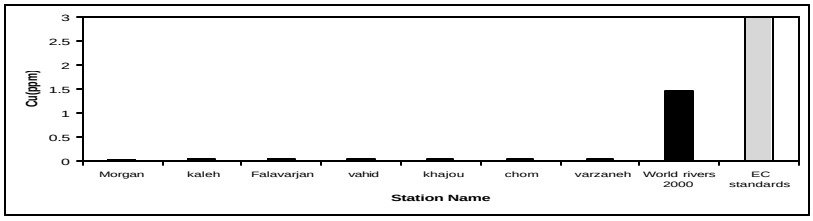

Fig. 2: Average concentration of Cu in different stations

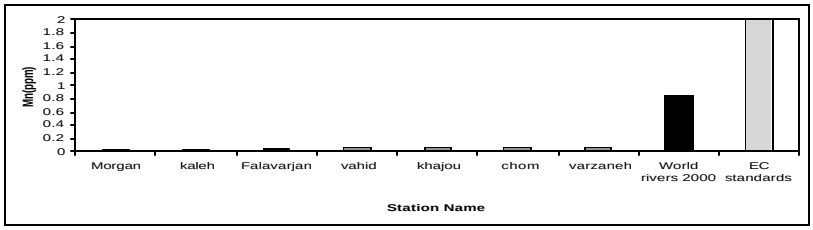

Fig. 3: Average concentration of Mn in different stations

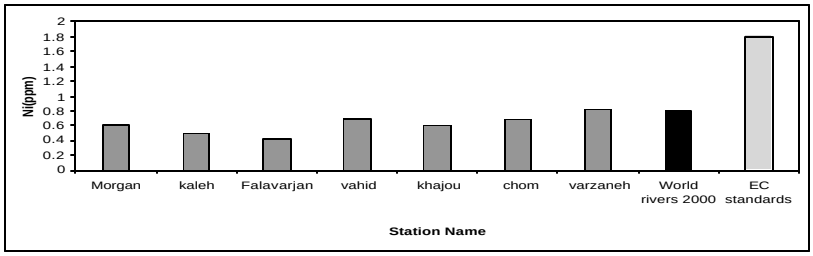

Fig. 4: Average concentration of Ni in different stations

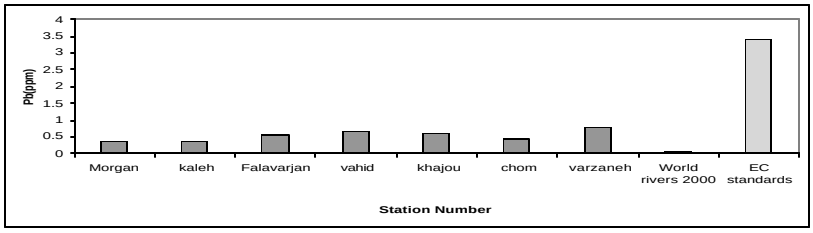

Fig. 5: Average concentration of Pb in different stations

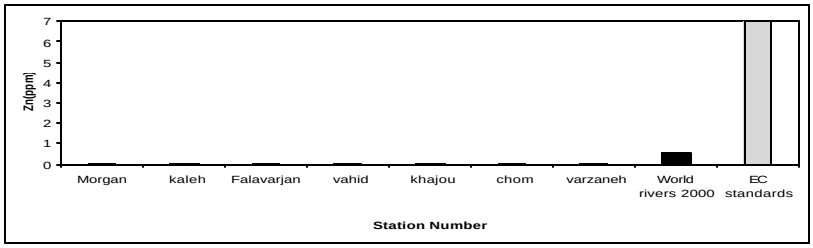

Fig. 6: Average concentration of Zn in different stations

The result clearly indicated that Heavy metal concentrations were commonly in the same range with world river averages reported by [15]. The maximal concentrations of these metals in autumn were 1.41 for Pb. In general in the last station (Pole Varzaneh) the highest amount of metals were observed. Mn was determined the highest in Pole chom and Pole Varzaneh in autumn. The result showed that there was no detectable Cd level present in water in Morgan station, thus there is Cd source in Pole kaleh. No major different in Zn concentration was observed in autumn.

At Morgan station south west of Isfahan. Wastewater discharges into the wells and river water, due to leak of a rural wastewater treatment system. At Pole-Chom discharge of the effluent from Isfahan wastewater treatment plant into the river takes place after this station. At Varzaneh city water is highly polluted due to the industrial, agricultural and municipal wastewater discharge into the river. The minimal and maximal concentrations of these metals in summer were 69.3–110.7, 1.7–118.3 and 5.5–70.3 ìg/l, for Zn, Pb and Cu, respectively.

According to Figures 1 to 6, both nickel and cadmium are higher than other metals compare to World Rivers [16] and EC standards [17], it can be because of using rechargeable batteries in the region. Pole Kaleh and Falavarjan are both farming and industrial area but the amount of metals are not notably high in this areas. The concentrations of dissolved metals are close to the values reported by other researchers [3] In agreement, the present study shows that some metal at sites are the higher than EC river water standards [16]. Observing the concentration and distribution of heavy metals can be helpful to find out the pollution sources, mainly in water systems: total median of variation in following heavy metal concentration on observed stations is 4 time sampled in different seasons will be shown and discussed according to Tables 2-5, there was insignificant variation during different seasons, however in station 2 and station 4 and 7 the amount of concentration of these elements was in maximum, but there was not nay specific and same trend in different stations. It is below water quality standards recommended by the European Community [16] as well. Concentration of Pb was in its minimum amount in station 3 and maximum amount in station 7. it can caused by some river shock or sewage during sampling period hat cause increase on sudden concentration changes on the other hand Cr concentration was maximum at 4th and 7th stations. Ni concentration was observed 0.41 to 1.09 mg/l that is higher than EC standards [17], it is 0.05 these increase and these over limitation perhaps were caused by some met logical industries and some galvanization workshops in the region which will have sewage effect to the river. Compare to other rivers [18-22], concentration of trace metals in Zayandeh Rood is high consequently an integrated plan is needed for pollution control in the region.

Table 6: Comparison of FAAS and ICP-AES by a linear regress

Element	Regression equation	X,Y pairs
Pb	Y= 1.211 + 0.98 X	7
Cd	Y= 0.122 + 1.044 X	7
Cu	Y= 0.377 + 0.980 X	7
Ni	Y = -0.101 + 1.001 X	7
Zn	Y= 0.372 + 1.83 X	7
Mn	Y= 1.229 + 0.823 X	7

Pole vahid, Pole khajou and Pole chom stations are located in Isfahan city with population of more than two million and received some solid wastes. One of the sources of pollution in agricultural wastewater can be fertilizers containing heavy metals and Fungicides, mainly consisting of copper compounds. The measured concentrations of Mn, Cu and Pb presented different profiles, suggesting different origins. The concentrations of Mn increased a little along the middle part of the river (stations 4 and 5), although high concentrations were also found in station 3 in winter.

Comparison of Metal Concentration Determination by AAS and lCP-AES: Several samples were digested and analyzed for heavy metals by both FAAS and the proposed method. The results obtained by the two methods were compared and good agreement was found between the results. The regression equations between the concentrations of different elements analyzed by two techniques are summarized in Table 6. Although FAAS is a conventional and popular method for determination of heavy metals, but it is time-consuming and tedious, while ICP-AES in a multi-elemental technique which offers the same results as FAAS in short time Analysis of heavy metals by ICP-AES can be used in water pollution studies, especially where the samples are collected from river areas or in such cases where variations of levels of heavy metals are being studied during day time and sampling period is limited.

CONCLUSIONS

Seasonal variations in the concentrations of selected heavy metals in Zayandeh River water were investigated. The major sources of pollution of the

Zayandeh rood river are industrial wastewaters, along with urban and agricultural runoff. The heavy metal pollution status of Zayandeh Rood River was not published before other information was only available in rare cases for example Akbari *et al*. (2007) were monitored irrigation performance in Isfahan region [9] and some other Persian publication are also published about Zayandeh rood river. The peak concentrations of highly toxic elements, such as Cd and Ni were observed to originate partly from local point sources in pole vahid station, which should be investigated closer.

The concentrations of heavy metals in different points of the river are different. The analysis shows the critical points of the river and also shows the points that continuous control should be done. The latter method of releasing heavy metals into the river is important especially where the river is a source for drinking water. A comparison with earlier investigations and as a result of the increased economic growth, population and living standards suggest that the concentrations of important water quality constituents are not rising. As a general conclusion, some important contaminated areas were identified in the zayandeh rood river, Average heavy metals changes in different stations and different seasons will show that Cd and Ni concentration was higher than EC standards.

REFERENCE

1. Sayari, A., S. Hamoudi and Y. Yang, 2005. Applications of pore-expanded malodorous silica, removal of heavy metal captions and organic pollutants from waste water, Chem. Mater., pp: 212-216.
2. Zheng Na, Qichao Wang, Zhongzhu Liang and Dongmei Zheng, 2008. Characterization of heavy metal concentrations in the sediments of three freshwater rivers in Huludao City, Northeast China. Environmental Pollution, in Press.
3. Wakida, F.T., D. Lara-Ruiz J. Temores-Pen˜a, J.G. Rodriguez-Ventura, C. Diaz and E. Garcia-Flores, 2008. Heavy metals in sediments of the Tecate River, Mexico. Environ Geol, 54: 637-642.
4. Li Feng, Y.M. Wen and P.T. Zhu, 2008. Bioavailability and Toxicity of Heavy Metals in a Heavily Polluted River, in PRD, China. Bulletin of Environmental Contamination and Toxicology, in Press.
5. Mendiguchíaa Carolina, Carlos Moreno, a and Manuel García-Vargasa, 2008. Evaluation of natural and anthropogenic influences on the Guadalquivir River (Spain) by dissolved heavy metals and nutrients. Chemosphere, pp: 1509-1517.
6. Charya Sridhara, N., C.T. Kamalaa and D. Samuel Suman Raj, 2008. Assessing risk of heavy metals from consuming food grown on sewage irrigated soils and food chain transfer Ecotoxicology and Environmental Safety. Bulletin of Environmental Contamination and Toxicology, 69: 513-524.
7. Talebi, S.M., 1998. Determination of lead associated with air- borne particulate matter by flame atomic absorption and wave-length dispersive X-ray fluorescence spectrometry. Environ. Anal. Chem., 72: 1-9.
8. Guéguen, C., R. Gilbin, M. Pardos and J. Dominik, 2004. Water toxicity and metal contamination assessment of a polluted river: the Upper Vistula River (Poland). Applied Geochemistry, 19: 153-162.
9. Akbari Mehdi, Norair Toomanian, Peter Droogers, Wim Bastiaanssen, Ambro Gieske, 2007. Monitoring irrigation performance in Esfahan, Iran, using NOAA satellite imagery. Agricultural Water Management, 88: 99-109.
10. Bruder,V., F. Lgrade, M.J.F. Lerosy, C. Coughanower and F. Enguehard, 2002. Application of a sequential extraction procedure to study the release of elements from municipal solid waste incineration bottom ash. Anal, Chim, Acta, 451: 258-295.
11. NI, J.L., C.C. Liu and S.J. Jiang, 2005. Determination of Ga,As,Ge,SeandSb in fly ash samples by ultrasonic slurry electro thermal vaporization ICP-MS. Anal, Chim, Acta, 550: 144-150.
12. US-EPA, 1991. Test Method for Evaluating of Solid Waste. SW 846, US Environmental Protection Agency, Cincinnati. OH.
13. Martin Theodore, D., 2003. Determination of trace elements in drinking water by axially viewed inductively coupled plasma-atomic emission spectrometry. National exposure research laboratory, office of research and development, US Environmental Protection Agency, Cincinnati, OH.
14. APHA, 1999. Standard Methods for the Examination of water and Wastewater. 20th Ed. American Public Health Association. Washington DC.
15. Martin, J.M. and M. Meybeck, 1979. Elemental mass balance of material carried by major world rivers. Mar Chem, 7: 173-206.

16. Gaillardet, J., J. Viers and B. Dupré, 2004. Trace elements in river waters, Surface and ground water, weathering and soils. Treatise on Geochemistry, 5: 234-240.
17. LAWA, 2006. Overview of quality standards of the EC, the international river basin communities and LAWA. German Working Group of the Federal States on water issues (LAWA).at:http://www.umweltbundesamt.de/wasser/themen/oberflaechengewaesser/ow_s2_2.htm#heavy.
18. Turgut C., 2003. The contamination with organ chlorine pesticides and heavy metals in surface water in Küçük Menderes River in Turkey. Environment International, 29: 29-32.
19. Cheung, K.C., B.H.T. Poon, C.Y. Lan and M.H. Wong, 2003. Assessment of metal and nutrient concentrations in river water and sediment collected from the cities in the Pearl River Delta, South China. Chemosphere, 52: 1431-1440.
20. Doong Ruey-an, Shih-hui Lee, Chun-chee Lee, Yuh-chang Sun and Shian-chee Wu, 2008. Characterization and composition of heavy metals and persistent organic pollutants in water and estuarine sediments from Gao-ping River, Taiwan. Marine Pollution Bulletin, 57: 846-857.
21. Li Feng, Y.M. Wen and P.T. Zhu, 2008. Bioavailability and Toxicity of Heavy Metals in a Heavily Polluted River, in PRD, China. Bulletin of Environmental Contamination and Toxicology, in Press.
22. Karamanis, D., K. Stamoulis, K. Ioannides and D. Patiris, 2008. Spatial and seasonal trends of natural radioactivity and heavy metals in river waters of Epirus, Macedonia and Thessalia. Desalination, 224: 250-260.