# Assessment of Toxic Heavy Metal Concentration and their Changes in *Zayande-rood* River, *Isfahan*, Iran

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**Abstract**

*Zayande-rood* is one of the most important rivers flowing in the central part of Iran. The river water is used for drinking, industrial and agricultural purposes. However, industries mushroomed on the river bank, viz. steel factory (*zovb-e-ahan*), power plants, refinery and petrochemical complexes and mining activities drain wastewater into the river. In this study, the concentrations of heavy metals (Cd, Cu, Mn, Fe, Zn, Pb, Ni, Cr, V, Mo and As) in the *Zayande-rood* river were determined. Samples were collected from 12 stations along the river from *Baghbahadoran* to *Isfahan* in autumn 2009. Heavy meta l concentrations were obtained after acid digestion and analysis was carried out by ICP-MS. The maximum concentrations of these metals were 314.15, 95.88, and 48.36 µg $l^{-1}$ for Fe, Al and Mn, respectively. The samples with maximum of elements concentration were obtained from after-pour of *zovb-e-ahan* wastewater, Falavarjan and pole Ghadir stations. The concentration of heavy metals in different stations of this river was different. The analysis shows the critical points of the river and also shows the points that continuous control should be done.



## 1. Introduction

Environmental pollution is one of the biggest challenges world-wide today. Heavy metals contamination is a major pollutant adversely contributing to imbalance the ecosystem. Industrial growth has further posed its immense ill effects to the ecosystems. Most environmental regulations have established limitations for total heavy metal concentration in waters so that they do not exceed the limit for the protection of the environment. However, pollutants are discharged into rivers and lakes, and leach into the soil and ground water or are emitted into air as particulate matter (Abernathy et al., 1984). Heavy metals are critical in this regard because of their easy uptake into the food chain and bioaccumulation processes (Beijer and Jernelov, 1986).

Trace elements in aquatic systems may be attributed to natural geologic sources or to past and present land uses. Although heavy metals may originate from natural sources, human activities such as mining, agriculture and urbanization can affect its concentration and spatial distribution (Varkouhi, 2007). Burgeoning population demands more and more water, food and energy which results in the expansion of industrial and agricultural activities. This complex phenomenon ultimately leads to increasing production of various pollutants. Heavy metals are some of the most important of such pollutants.

*Zayande-rood* is one of the most important rivers flowing in the central part of Iran. The main sources of pollution of the *Zayande-rood* river are urban, agricultural and industrial waste-waters. Industrial waste-waters and sewage of metropolitan centers, small electroplating workshops, repair shops, hospitals and medical and scientific laboratories, as well as surface run-off of cities are main sources of such urban waste-waters (Babich and Stotsky, 1982). The industrial waste-water is discharged directly into the *Zayande-rood* river without any remediation. Only a simple physical screening is being performed. The turbulence of the water stream in winter is higher, because the seasonal floods lead to disturbances in the river base. Suspension of sediments into the water body may increase the metal concentration in the water. In addition, heavy rainfall leads to farm drainage. Large amounts of pesticides containing metal compounds are brought via surface run-off from the farms to the river, contributing heavily to the agricultural pollution (Rauret et al., 1988). The major sources of pollution in agricultural waste-water are fertilizers containing heavy metals such as Cd, Pb, Cr, Zn, Cu and Ni. Fungicides and algaecides used in fish farming are other sources of pollutants, mainly consisting of copper compounds (Spencer and Green, 1981).

In this study, concentrations of heavy metals were determined at 12 different stations of important industrial areas located upstream and downstream along the *Zayande-rood* river in *Isfahan* province of Iran during autumn 2009.

## 2. Materials and Methods

### *2.1. Study site*

*Isfahan* province was chosen for this study, because this is one of the most important industrial centers of Iran. The river source is located in Koohrang Mountains, and passes

through two provinces, *Chaharmohal bakhtiary* and *Isfahan*. The river at the end discharges to the *Gavkhooni* wetland. The river water is used for drinking, industrial and agricultural purposes. There are different kinds of industries in this province, such as power plants, steel factory (*zovb-e-ahan*), refinery and petrochemical complexes and mining activities, pipe, steel, paper and paint production plants, as well as food, beverage and dairy industries. From these sources heavy metals (Cu, Fe, Cd, Pb, Zn, Cr and Ni) leach into the waters (Vernet, 1993).

*2.2. Selection of sampling station*

The watershed of *Zayande-rood* river is situated in the middle of the central plateau of Iran between $50^{0}02^{'}$ and $53^{0}24'$ E longitude, and $31^{0}11^{'}$ and $33^{0}42^{'}$ N latitudes covering an area of about 41550 $km^2$ with an average altitude of 2514 m above sea level. It is the only permanent river in this basin. It originates from the eastern slopes of *Zardkouh-e-bakhtiari* mount in central *Zagros* and takes its course in south-west to north-east direction down to *Zayande-rood* dam (Aghanabati, 2004).

Concentrations of heavy metals in the river were measured. First, essential information about morphology and hydrology of river was obtained and the sources of pollution identified. According to this information, 12 sampling stations were chosen along the river (Table 1 and Figure 1). In selecting these stations, the following criteria were considered: slope of the river bank, route of the river, location of industries and their waste outlets, and accessibility for sampling (Jafarzadeh and Morovaty, 1996).

Table 1: Name and coordinate of sampling stations

| Station number | Name of station | Y | X |
|---|---|---|---|
| 1 | Zamankhan Bridge | 3594709 | 490265 |
| 2 | Chame Yousefali | 3589860 | 502000 |
| 3 | Morekan Bridge | 3584374 | 514608 |
| 4 | Baghbahadoran | 3582928 | 517986 |
| 5 | After baghbahadoran | 3582386 | 522015 |
| 6 | Cham aseman dam | 3582114 | 520033 |
| 7 | Zarinshahr Bridge | 3583159 | 532228 |
| 8 | Before-pour of *zovb-e-ahan* sewage | 3580988 | 539731 |
| 9 | After-pour of *zovb-e-ahan* sewage | 3580591 | 541015 |
| 10 | Diziche | 3582210 | 549533 |
| 11 | Falavarjan | 3602421 | 548721 |
| 12 | Ghadir Bridge | 3610851 | 565899 |

*2.3. Reagents*

All reagents were of analytical grade. De-ionized water, further purified using a Milli Q System (Millipore, Molsheim, France ,(was used throughout. Stock standard solutions of metals (1000 mg $ml^{-1}$) were obtained by dissolving the pure metals. Standard solutions were employed for calibration in the analysis of extracts. Calibration standards made in 1% v/v $HNO_3$ were employed for analysis of digests. $HNO_3$, extra pure and standard solution of elements were purchased from Merck Company.

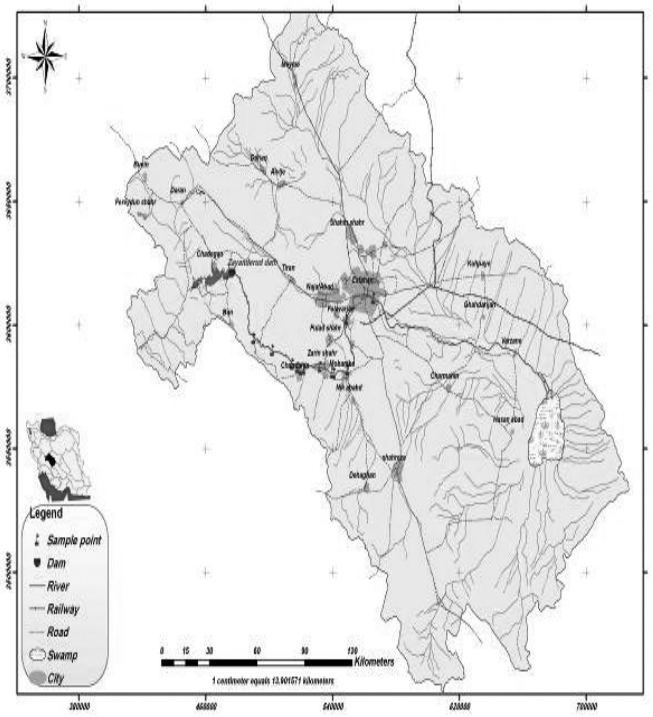


Figure 1: The map of *Isfahan* province and sampling stations

*2.4. Sample collection and analysis*

Water samples were collected in November 2009. At each station three water samples were collected using 1-l polyethylene acid-washed containers (Csuros, 1994), and the samples' average was selected for analysis. Meanwhile, in order to determine the enrichment coefficient and pollution rate, three more water samples were chosen at non-polluted (upstream) parts of the river.

The containers were rinsed with 5% nitric acid and distilled water, and were washed with river water before sampling. Samples were acidified with 1-2 ml of concentrated nitric acid (pH<2). The samples were transported to the laboratory according to standard protocols. Before analysis, samples taken at the same water depth from one station were pooled. Analysis was carried out by inductively coupled plasma mass spectrometry (ICP-MS, Varian, 710 ES). Samples were quantified by using standard solutions of the stock solution of soluble salts of the respective metal. Distilled water was used for dilution of the samples.

*2.5. Statistical analysis*

All analyses were performed on triplicate samples and data (presented as mean±SD) were subjected to analysis of variance (ANOVA). The data were tested for homogeneity of variances at the significance level of $p<0.05$ and probability values of less than 0.05 were considered as statistically significant (one-way ANOVA). SPSS version 11.5 (SPSS Inc., Chicago, IL, USA) was used for statistical analysis.

## 3. Results and Discussion

Total concentration of heavy metals and their changes at twelve stations are shown in Table 2.

The mean concentrations of heavy metals at each of the stations were significantly different with other ($p$<0.01). Table 2 demonstrates that in all sampling stations, the mean concentrations of all heavy metals were significant and consistent. The maximum amount of total concentration for Fe, Al and Mn was very higher than other elements. The concentration of these elements was 314.15, 95.88 and 48.36 µg $l^{-1}$, respectively. Zamankhan bridge station was selected for comparison because it is very far from human activities in upstream. In sample 1 (pole Zamankhan station) heavy metals did not show high concentration than other stations. The samples that had maximum concentration of elements were related to station number 9 (after-pour of *zovb-e-ahan* wastewater), 11 (Falavarjan) and 12 (Ghadir Bridge).

Table 2: Concentration (µg $l^{-1}$) of heavy metals at twelve stations

| Station number | Pb | Ni | As | Cu | Fe | Zn | Al | Cr | V | Mo | Mn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.40 | 2.90 | 0.70 | 1.50 | 59.79 | 2.10 | 37.60 | 0.60 | 0.80 | 0.90 | 37.40 |
| 2 | 1.50 | 1.10 | 0.90 | 1.70 | 81.00 | 2.40 | 74.00 | 0.80 | 1.60 | 1.10 | 45.67 |
| 3 | 160.00 | 0.90 | 0.90 | 1.20 | 104.00 | 1.60 | 88.00 | 0.80 | 1.55 | 1.00 | 52.25 |
| 4 | 3.20 | 1.50 | 0.90 | 1.80 | 92.00 | 1.80 | 90.00 | 0.80 | 1.50 | 1.00 | 51.77 |
| 5 | 2.10 | 1.60 | 0.90 | 1.60 | 102.00 | 2.10 | 94.00 | 0.95 | 1.60 | 1.00 | 54.30 |
| 6 | 1.40 | 3.60 | 0.90 | 1.20 | 124.00 | 2.20 | 89.00 | 0.70 | 1.80 | 1.00 | 52.03 |
| 7 | 3.10 | 14.50 | 0.90 | 3.00 | 794.00 | 5.50 | 91.00 | 0.70 | 0.90 | 0.90 | 53.33 |
| 8 | 0.60 | 0.40 | 0.90 | 1.50 | 1036.00 | 3.70 | 99.00 | 0.60 | 2.30 | 1.00 | 59.04 |
| 9 | 0.60 | 0.40 | 1.00 | 3.80 | 945.00 | 4.30 | 94.00 | 0.70 | 2.10 | 1.10 | 56.27 |
| 10 | 1.30 | 4.80 | 1.10 | 1.80 | 221.00 | 8.30 | 173.00 | 0.65 | 1.60 | 0.90 | 47.92 |
| 11 | 1.00 | 4.85 | 1.10 | 1.95 | 150.00 | 7.50 | 143.00 | 0.62 | 1.90 | 1.10 | 38.90 |
| 12 | 0.70 | 4.90 | 1.20 | 2.20 | 61.00 | 4.60 | 78.00 | 0.60 | 2.10 | 1.20 | 31.48 |
| Mean | 14.74 | 3.45 | 0.95 | 1.94 | 314.15 | 3.84 | 95.88 | 0.71 | 1.65 | 1.02 | 48.36 |

Data are presented as mean±SD of three experiments

## 4. Conclusion

The study shows the critical points of heavy metal concentration in the river and also shows the points that require continuous control and monitoring. The release of heavy metals into the river is important especially where the river is a source of drinking and irrigation water. In essence, the present investigation on pollution of the *Zayande-rood* river provides a typical example of environmental problems in a country like Iran. The study recommends that there must be an appropriate government policy to combat this problem on an urgent basis.

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