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Assessing and Ranking Heavy Metal Effects on Zayanderood River of Iran in Terms of MADM

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Abstract Zayanderood is one of the most important river of Iran from west to east. The river source is located in Koohrang Mountains. The river passes through two provinces, Chaharmahal-Bakhtiary and esfahan. The river at the end discharges to the Govkhooni wetland. The river water is used for drinking, industrial and agricultural purposes. The determination of pollutants as heavy metals and other chemical parameters throughout the river is important and has a great role in the control of ecological condition of 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. In the present work, ICP-MS as a multi-elemental technique has been used for the determination of heavy metals. the concentration of heavy metals in different stations of this river was different. The analysis shows the critical points of the river and also shown the points that continuous control should be done. In this paper, using multiple attribute decision making (MADM) is proposed. MADM problem is management science technique, which is popularly used to rank the priority of alternatives with respect to their competing attributes. Weights from the core of MADM: it is obvious that different weight lead to various evaluation results and decisions. The proposed model is applied for finding the best option from all the feasible alternatives.

1. Introduction

Environmental pollution is one of the biggest challenges world-wild today. Heavy metal contamination is 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 protection of the environment. However, pollutants are

Key words and phrases. Heavy metals; Water pollution; Enrichment; Zayanderood river; Multiple Attribute Decision Making (MADM).

discharged into rivers and lakes, and leach into the soil and ground water or are emitted into air as particulate matter. 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 of the most environmental pollutant which accumulates in living organisms. Its cumulative poisoning effects are serious hematological and brain damage, anemia and kidney malfunctioning. Heavy metals in different river are most investigated recently. 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 waste-water. Soils irrigated by waste water accumulate: Heavy metal such as Cr, Zn, Pb, Cd, Ni, etc. in surface soil. Zayanderood river is one of the most important rivers flowing in the central part of Iran. the main source of pollution of the Zayanderood river are urban, agricultural and industrial waste-waters. Industrial waste-water and sewage of metropolitan centers, small electroplating workshops, repair shops, hospitals and medical and scientific laboratories, as well as surface run-off cities are main sources of such urban waste-waters. The waste-water is discharged directly into the Zayanderood river without any remediation. The turbulence of the water stream in winter is higher, because the seasonal floods lead to disturbances in the 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 amount of pesticides containing metal compounds are brought via surface run-off from the farms to the river, contributing heavily to the agricultural pollution. 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. In this study concentration of heavy metals were determined at 12 different stations of important industries areas located upstream and downstream along at the Zayanderood river in Esfahan province of Iran during November 2008 to August 2009.

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). 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.

All reagents were of analytical grade. De-ionized water, further purified using a mili Q system (Millipore, Molsheim, France), and was used throughout. Stock standard solutions of metals (1000 mg/ml) 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 HNO3 were employed for analysis of digests. HNO3 extra pure and standard solution of elements was purchased from MWRK company. Most of these studies have used major of pollution in

Table 1. Name and characterization of the sampling stations

	Station name	Y	X	Reason of station selection
1	Pole Zaman Khan (witnesss or blank sample)	3594709	490265	Determination of geochemical background- this station is none- contaminated because high discharge, high slope with transparent water
2	Cham ypsefali	3589860	502000	Investigation of heavy metals with natural origins,urban and agricultural waste waters
3	Pole morkan	3584374	514608	Rural domestic and agricultural waste waters,Domestic industries
4	Bagh bahadoran	3582928	517986	Urban and agricultural waste waters
5	Pole kale (after bagh bahadoran)	3582386	522015	Urban and agricultiral waste waters metallic industries
6	Cham aseman dam	3582114	520033	Drinkable water of esfahan
7	Pole zarinshahr	3583159	532228	Industrial,Urban and agricultural waste waters metallic and military industries
8	Before pour of iron factory waste waters	3580988	539731	Exact investigation of heavy metal concentration that probably inter to zayanderood from this station
9	After pour of iron iron factory waste waters	3580591	541015	Zovbe ahan and zarin shahr waste water and lands that irrigated with Zovbe ahan waste water
10	Diziche	3582210	549533	Sepahan cement factory - metallic industries
11	Pole falavarjan	3602421	548721	Urban and agricultural waste waters and mining
12	Pole ghadir	3610851	565899	Control station between entrance and exit station

Y, X: Geographical coordinate

agricultural waste-water. To the best of our knowledge, Multiple Attribute Decision Making (MADM) has not employed to study the apicultural performance of Zayanderood river, although it has been used to compare different stations of important industries area. In this paper, MADM helps provide a comparative picture of performance of selected Zayanderood river. Sample collection and analysis discussed in section 2, discussed in section 3, Topsis method and illustrate our proposed method with an example in section 4 and final section is summary.

2. Sample Collection and Analysis

Water samples were collected in November 2008 to August 2009. At each station 3 water samples were collected using 1-1 polyethylene acid-washed containers, 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<). The samples were transported to the laboratory according to standard protocols. Before analysis, sample taken at the same water depth from one station were pooled. Analysis was carried out by inductively coupled plasma mass spectrometry (ICP-MS, varian, 710ES). Samples were quantified by using standard solutions of the stock solution salts of the respective metal. Distilled water was used for dilution of the samples.

2.1. *Statistical Analysis*

all analysis 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. Multiple Attribute Decision Making (MADM)

Multiple attribute decision making has been one of the fastest growing areas during the last decade depending on the changing. Decision marker(s) need a decision aid to decide between the alternatives and mainly excel less preferable alternatives fast. With the help of computers the decision making methods have found great acceptance in all area of the decision making processes. Since multiple attribute decision making (MADM) has found acceptance in area of operation research and management science, the discipline usage has increased significantly, the application of MADM methods has considerably become easier for the users the decision makers. In discrete alternative multiple attribute decision problems; the primary concern for the decision aid is the following:

(i) choosing the most preferred alternative to the decision maker (DM),
(ii) ranking alternative in order of importance for selection problems, or
(iii) screening alternative for the final decision.

The general concepts of domination structures and non-dominated solutions play an important role in describing the decision problems and the decision marker's revealed preferences describes above.= So far, various approaches have been developed as the decision aid. That is, for many such problems, the decision maker wants to solve a multiple attribute decision making (MADM) problem. A MADM problem can be concisely expressed in matrix format as:

$$\begin{array}{ccccc} & C_1 & C_2 & \dots & C_n \\ A_1 & x_{11} & x_{12} & \dots & x_{1n} \\ A_2 & x_{21} & x_{22} & \dots & x_{2n} \\ \vdots & \vdots & \vdots & \dots & \vdots \\ A_m & x_{m1} & x_{m2} & \dots & x_{mn} \end{array}$$

$$W = \{w_1, w_2, \dots, w_n\}$$

Where $A_1,A_2,\ldots,A_m$ are possible alternatives among which decision makers have to choose, $x_1,x_2,\ldots,x_n$ are attribute with which alternative performance are measured, x_{ij} is the rating of alternatives A_i with respect to attribute x_j, w_j is the weight of attribute C_j.

The main steps of multiple attribute decision making are the following:

(i) Establishing system evaluation attribute that relate system capabilities to goal.
(ii) Developing alternative systems attaining the goal(generating alternatives).
(iii) Evaluation alternatives in terms of attribute (the value of the attribute function).
(iv) Applying a normative multi attribute analysis method.
(v) Accepting one alternative as "optimal" (preferred).
(vi) If the final solution is not accepted, gather new information and into the next interaction of multiple attribute optimization.

Step (i) and (v) are preformed at the upper level, where decision makers have the central role, and the other steps are mostly engineering task. For step (iv), a decision maker should express his/her preference by similarity to ideal solution (TOPSIS), one of known classical MADM method, was first developed by Hwang and Yoon for solving a MADM problem. TOPSIS, known as one of the most classical MADM methods, is based on the idea, that the chosen alternative should have the shortest distance from the positive ideal solution and on the other side the farthest distance of the negative ideal solution. The TOPSIS method will be applied to a case study, which is described in detail. In classical MADM methods, the rating and the weight of the attribute are known precisely. A survey of the methods has been presented in Hwang and Yoon [1]. In the process of Topsis, the performance rating and the weights of the attribute are given as exact values.

4. TOPSIS method

TOPSIS (technique for order preference by similarity to an ideal solution) method is presented in Chen and Hwang [10], with reference to Hwaang and Yoon. TOPSIS is a multiple attribute method to identify solutions from a finite set of alternatives. The basic principle is that the chosen alternative should have the shortest distance from the positive ideal solution and farthest distance from the negative ideal solution. The procedure of TOPSIS can be expressed in a series of step:

(i) Calculate the normalize decision matrix. The normalize value n_{ij} is calculated as:

$$n_{ij} = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{m} x_{ij}^2}}, \quad i = 1,\ldots m, j = 1,\ldots,n$$

(ii) Calculate the weighted normalized decision matrix. The weighted normalized value v_{ij} is calculated as:

$$v_{ij} = w_j n_{ij}, \quad i = 1, \dots, m, \ j = 1, \dots, n$$

where w_{ij} is the weight of the i-th attribute, and $\sum_{j=1}^{n} w_j = 1$.

(iii) Determine the positive ideal and negative ideal solution:

$$A^+ = \{v_1^+, \dots, v_n^+\} = \left\{ \left(\underset{j}{\text{Max}} v_{ij} / i \in I \right), \left(\underset{j}{\text{Min}} v_{ij} / i \in J \right) \right\},$$

$$A^- = \{v_1^-, \dots, v_n^-\} = \left\{ \left(\underset{j}{\text{Min}} v_{ij} / i \in I \right), \left(\underset{j}{\text{Max}} v_{ij} / i \in J \right) \right\}$$

where I is associated with benefit attribute, and J is associated with cost attribute.

(iv) Calculate the separation from the positive ideal solution is given as:

$$d_i^+ = \left\{ \sum_{j=1}^{n} (v_{ij} - v_j^+)^2 \right\}^{\frac{1}{2}}, \quad i = 1, \dots, m$$

Similarity, the separation from the negative ideal solution is given as:

$$d_i^- = \left\{ \sum_{j=1}^{n} (v_{ij} - v_j^-)^2 \right\}^{\frac{1}{2}}, \quad i = 1, \dots, m$$

(v) Calculate the relative closeness to the ideal solution. The relative closeness of the alternative A_i with respect to A^+ is defined as:

$$R_i = \frac{d_i^-}{(d_i^+ + d_i^-)}, \quad i = 1, \dots, m$$

Since $d_i^- \geq 0$ and $d_j^+ \geq 0$ than, clearly, $R_i \in [0, 1]$.

(vi) rank the preference order, for ranking alternatives using this index; we can rank alternatives in decreasing order.

4.1. *Discussion and Results*

Total concentration of heavy metals and their changes at 12 stations are shown in Table 2. The mass 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 microgram/l, respectively. Zamankhan bridge station was selected for comparison because it is very far from human activities in upstream. In sample 1 (Pole Zaman Khan station) heavy metals did not show high concentration than other stations. The sample that had maximum concentration of elements were related to station number 9 (after pour of Zovbe-ahan waste-water), 11 (falavarjan) and 12 (ghadir bridge).

Table 2. Heavy metals concentration in sampling station (ppb)

Site	V	Cr	Mo	Zn	As	Cu	Al	Mn	Fe	Ni	Pb
W1	0.80	0.60	0.90	2.10	0.70	1.50	37.60	37.40	59.79	2.90	1.40
W2	1.60	0.80	1.10	2.40	0.90	1.70	74.00	45.67	81.00	1.10	1.50
W3	1.55	0.80	1.00	1.60	0.90	1.20	88.00	52.25	104.00	0.90	1.60
W4	1.50	0.80	1.00	1.80	0.90	1.80	90.00	51.77	92.00	1.50	3.20
W5	1.60	0.95	1.00	2.10	0.90	1.60	94.00	54.30	102.00	1.60	2.10
W6	1.80	0.70	1.00	2.20	0.90	1.20	89.00	52.03	124.00	3.60	1.40
W7	0.90	0.70	0.90	2.50	0.90	3.00	91.00	53.33	794.00	14.50	3.10
W8	2.30	0.60	1.00	3.70	0.90	1.50	99.00	59.04	1036.00	0.40	0.60
W9	2.10	0.70	1.10	4.30	1.00	3.80	94.00	56.27	945.00	0.40	0.60
W10	1.60	0.65	0.90	8.30	1.10	1.80	173.00	47.92	221.00	4.80	1.30
W11	1.90	0.62	1.10	7.50	1.10	1.95	143.00	38.90	150.00	4.85	1.00
W12	2.10	0.60	1.20	4.60	1.20	2.20	78.00	31.48	61.00	4.90	0.70

Since Zayanderood River's water is used in some areas to supply drinking water, it's necessary to eliminate or purge it's heavy metals. In so doing, following mechanisms can be taken advantage of:

(i) *Biofilters*: these are considered to be important environmental filters. In these filters,bacteria and microorganisms which can absorb heavy metals are stabilized on specific layers made of sand. With water getting through the filter,bacterial activity can absorb and thus filter out heavy metals.

(ii) *Zeolits*: given abundant zeolits sources available in Iran (e.g. clinopetilolit), they can be used to physically filter out heavy metals from water. Zeolits are hydrated aluminosilicate cations of alkaline and alkaline-earth metals with 3d lattices which are now economically used to filter out harmful and toxic pollutants(e.g. heavy metals, ammoniac and radioisotopes such as cesium all strontium) from municipal, industrial and nuclear sewage and waste waters.

(iii) *Absorbing plants*: such plants can absorb and bioaccumulate heavy metals, and thus help refining soils polluted with organic and mineral pollutants. This mechanism is easily implemented and relatively cheap, and can be used in large scale. In this method, once the plant is removed, heavy metals absorbed by it are removed from the environment as well.

(iv) *Chemical methods*: i.e. using water treatment lagoons so that heavy metals get precipitated.

(v) *Activated carbon*: it can absorb or reduce heavy metal content of water.

Table 3. The normalized decision matrix

Site	V	Cr	Mo	Zn	As	Cu	Al	Mn	Fe	Ni	Pb
W1	0.13572	0.24145	0.25455	0.13729	0.21086	0.20923	0.10726	0.220202	0.03615	0.16488	0.230501
W2	0.27144	0.32194	0.31112	0.156909	0.27111	0.23713	0.21111	0.26889	0.04905	0.06254	0.24696
W3	0.26296	0.32194	0.28284	0.104606	0.27111	0.16739	0.25104	0.30763	0.06297	0.05117	0.26343
W4	0.25448	0.32194	0.28284	0.11768	0.27111	0.25108	0.25675	0.304809	0.05571	0.08228	0.52686
W5	0.27144	0.382303	0.28284	0.13729	0.27111	0.22318	0.26816	0.319705	0.06176	0.09097	0.34575
W6	0.30538	0.28169	0.28284	0.14383	0.27111	0.16739	0.253901	0.30633	0.07508	0.20468	0.230501
W7	0.15269	0.28169	0.25455	0.35958	0.27111	0.41847	0.259607	0.31399	0.48081	0.82441	0.51039
W8	0.390209	0.24145	0.28284	0.241902	0.27111	0.20923	0.28243	0.34761	0.62735	0.02274	0.09878
W9	0.35627	0.28169	0.31112	0.28112	0.30123	0.53007	0.26816	0.331304	0.57225	0.02274	0.09878
W10	0.27144	0.26157	0.25455	0.54264	0.33136	0.25108	0.49353	0.28214	0.13382	0.27291	0.21403
W11	0.32234	0.249503	0.31112	0.49034	0.33136	0.272009	0.40795	0.22903	0.09083	0.27575	0.16464
W12	0.35627	0.24145	0.33941	0.30074	0.36148	0.30688	0.22252	0.18534	0.03693	0.27859	0.11525

$W = (w_1, \dots, w_{11}) = (0.00267, 0.00115, 0.00165, 0.00624, 0.00154, 0.00314, 0.1558, 0.0786, 0.7409, 0.00561, 0.0025)$

Table 4. The weighted normalized decision matrix

Site	V	Cr	Mo	Zn	As	Cu	Al	Mn	Fe	Ni	Pb
W1	0.000362	0.000277	0.000420	0.000856	0.000324	0.000656	0.01671	0.01730	0.02678	0.00092	0.00057
W2	0.000724	0.000370	0.000513	0.000972	0.000417	0.000744	0.03289	0.02113	0.03634	0.00035	0.00061
W3	0.000702	0.000370	0.000466	0.000652	0.000417	0.000525	0.03911	0.02417	0.04665	0.00028	0.00065
W4	0.000679	0.000370	0.000466	0.000734	0.000417	0.000788	0.04000	0.02395	0.04127	0.00046	0.00131
W5	0.000724	0.000439	0.000466	0.000856	0.000417	0.000700	0.04177	0.02512	0.04575	0.00051	0.00086
W6	0.000815	0.000323	0.000466	0.000897	0.000417	0.000525	0.03955	0.02407	0.05562	0.00114	0.00057
W7	0.000407	0.000323	0.000420	0.002243	0.000417	0.001313	0.04044	0.02467	0.35623	0.00462	0.00127
W8	0.001041	0.000277	0.000466	0.001509	0.000417	0.000656	0.04400	0.02732	0.46480	0.00012	0.00024
W9	0.000951	0.000323	0.000513	0.000175	0.000463	0.001664	0.04177	0.02604	0.42398	0.00012	0.00024
W10	0.000724	0.000300	0.000420	0.003386	0.000510	0.000788	0.07689	0.02217	0.09914	0.00153	0.00053
W11	0.000860	0.000286	0.000513	0.003059	0.000510	0.000854	0.06355	0.01800	0.06729	0.00154	0.00041
W12	0.000951	0.000277	0.000560	0.001876	0.000556	0.000963	0.03466	0.01456	0.02736	0.00156	0.00028

$A^+ = \{0.001041, 0.000439, 0.000560, 0.003386, 0.000556, 0.001664, 0.07689, 0.02732, 0.46480, 0.00462, 0.00131\}$

$A^- = \{0.000362, 0.000277, 0.000420, 0.000175, 0.000324, 0.000525, 0.01671, 0.01456, 0.02678, 0.00012, 0.00024\}$

$d_1^+ = 0.44226$, $d_2^+ = 0.43077$, $d_3^+ = 0.41983$, $d_4^+ = 0.42546$, $d_5^+ = 0.42054$, $d_6^+ = 0.41090$,

$d_7^+ = 0.11451$, $d_8^+ = 0.033255$, $d_9^+ = 0.054141$, $d_{10}^+ = 0.0366043$, $d_{11}^+ = 0.397850$, $d_{12}^+ = 0.441335$,

$d_1^- = 0.002954$, $d_2^- = 0.019910$, $d_3^- = 0.031430$, $d_4^- = 0.028997$, $d_5^- = 0.033159$, $d_6^- = 0.038004$,

$d_7^- = 0.330497$, $d_8^- = 0.439054$, $d_9^- = 0.398156$, $d_{10}^- = 0.094480$, $d_{11}^- = 0.062101$, $d_{12}^- = 0.018108$.

Table 5. Ranking

	Station name	R_i $(i = 1, \ldots, 12)$	
1	Pole Zaman Khan (witnesses or blank sample)	0.006635	12
2	Cham ypsefali	0.044177	10
3	Pole morkan	0.069649	8
4	Bagh bahadoran	0.063805	9
5	Pole kale (after bagh bahadoran)	0.073085	7
6	Cham aseman dam	0.084659	6
7	Pole zarinshahr	0.772678	3
8	Before pour of iron factory waste waters	0.929590	1
9	After pour of iron factory waste waters	0.880297	2
10	Diziche	0.205158	4
11	Pole falavarjan	0.135016	5
12	Pole ghadir	0.039412	11

5. Summary

Decision making problem is the process of finding the best option from all the feasible alternatives. In this paper, multiple attribute models for the most preferable choice, technique for order preference by similarity to deal solution (TOPSIS) approach has been dealt with. The data (attribute) are often not so deterministic, the aim of this paper used the TOPSIS method and decision making problem used to compare different stations performance of Zayanderood River.

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