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## *Table of Contents*

Title	Page
<p>■ <b>A Performance Comparison of Three Computer Algorithms in the Selection of Best Protected Areas (Case Study: Mazandaran Province of Iran)</b> <i>Azade Mehri, Abdolrassoul Salmanmahiny, Seyed Hamed Mirkarimi, Hamid Reza Rezaei</i></p>	1
<p>■ <b>An Investigation on Cd Accumulation Potential in <i>Myrtus communis</i> and <i>Pinus brutia</i></b> <i>Asghar Mosleh Arany, Mehri Khosravi, Hamid Reza Azimzadeh, Hamid Sovdaeizadeh, Asghar Sapahvand</i></p>	4
<p>■ <b>Comparison of Carbon Sequestration of <i>Astragalus gossypinus</i> and <i>Dactylis glomerata</i> Species in Hezarjarib Mountainous Rangelands, Behshahr</b> <i>Marziyeh Hassannejad, Reza Tamartash, Mohammad Reza Tatian</i></p>	7
<p>■ <b>Long-term Effects of Logging Damages on Quality of Residual Trees in the Asalem Nav Forest</b> <i>Farzam Tavankar, Amir Eslam Bonyad</i></p>	10
<p>■ <b>The Application of GIS in Site Selection and Space-Place Analysis of Pollution and Air Pollutant Sources in Metropolitan Kermanshah</b> <i>Hamidreza Jafari, Sirus Hassanpour, Leila Rahili KHorasani, Ahmad Pourahmad</i></p>	13
<p>■ <b>An Investigation on the Status of Troposphere NO<sub>2</sub> Over Iran During 2004 to 2012</b> <i>Zahra Shariepour, Abbasali Aliakbari Bidokhti</i></p>	16
<p>■ <b>Optimization of DRASTIC and SINTACS Models According to Geographical Information System with the Use of Analytical Hierarchy Process (AHP) (Case Study: Andimeshk Plain)</b> <i>Mehrnaz Asefi, Feridon Radmanesh, Heidar Zarei</i></p>	19
<p>■ <b>A Feasibility Study on Qualitative Indicators in Isfahan City</b> <i>Nasim Sharifianpur, Shahrzad Faryadi</i></p>	22
<p>■ <b>Environmental Risk Assessment of Gotvand-Olia Dam at Operational Phase Using the Integrated Method of Environmental Failure Mode and Effects Analysis (EFMEA) and Preliminary Hazard Analysis</b> <i>Seyed Ali Jozi, Seyede Hamideh Seyfossadat</i></p>	25
<p>■ <b>Game Theoretic Insights for Sustainable Common Poll Water Resources Governance (Case Study: Lake Urmia Water Conflict)</b> <i>Amir Safaee, Bahram Malek Mohammadi</i></p>	28
<p>■ <b>Hydrogeochemical Analysis of Biddkhan Stream of Bardsir (Southeast Iran) Using Principal Component and Cluster Analyses</b> <i>Sara Sheikhfakhradini, Ahmad Abbasnejad</i></p>	31
<p>■ <b>Uptake and Removal Capability of Toxic Heavy Metals From the Industrial Discharge of Mobarakeh Steel Complex by Metal Accumulating Plants</b> <i>Seyed Majid Ghaderian, Samaneh Nosouhi</i></p>	34
<p>■ <b>Optimization of Malachite Green Biosorption by Green Microalgae from Aqueous Solutions</b> <i>Masoud Kousha, Omidvar Farhadian, Salar Dorafshan, Nasrollah Mahboobi Sootfani</i></p>	37
<p>■ <b>Simultaneous Application of Fenton – Electrochemical Reactor for Removal of Organic Loading in Biological Waste Sludge</b> <i>Gagik Badalians Gholikandi, Hamidreza Masihi, Maryam Mirabi</i></p>	40
<p>■ <b>Removal of Cd<sup>2+</sup> and Pb<sup>2+</sup> Ions from Aqueous Solutions Using Iranian Natural Zeolite and Sepiolite</b> <i>Seyedeh Safieh Hashemian Ghahfarokhi, Ahmad Landi, Hossein Khademi, Saeid Hojati</i></p>	43
<p>■ <b>Heavy Metals Concentration Changes during Vermicomposting of Organic Wastesq</b> <i>Seyedeh Maryam Kharrazi, Habibollah Younesi, Javad Abedini-Torghabeh</i></p>	46
<p>■ <b>Anaerobic Treatment by UASB Reactor and Aerobic Biodegradability Test of Cutting Oil Sewage</b> <i>Alireza Nazari Alavi, Ali Akbar Sajadi, Mohammad Mirzaei, Hamed Hasanian</i></p>	49
<p>■ <b>Evaluation of Scenarios in Artificial Recharge With Treated Wastewater on the Quantity and Quality of the Shahrekord Aquifer</b> <i>Reza Lalehzari, Sayyed Hassan Tabatabaei, Majid Khayat-kholghi, Nabiallah Yarali, Ali Akbar Saba</i></p>	52
<p>■ <b>Numerical Simulation of Plume Rise in Neutral Atmospheric Stability Condition</b> <i>Khosro Ashrafi, Majid Shafiepour, Hadis Abbaszadeh</i></p>	55
<p>■ <b>An Estimation on Mortality Cost Through Air Pollution in Isfahan City</b> <i>Gholam Hossain Kiani, Fateme Yari, Hadi Amiri</i></p>	58
<p>■ <b>Determine the Concentration and Sources of HCHs Isomers In Sediments of Siahrud River (Qaemshahr, Iran)</b> <i>Kamyar Taheri, Nader Bahrami Far, Hamid Reza Moradi</i></p>	61

## A Performance Comparison of Three Computer Algorithms in the Selection of Best Protected Areas (Case Study: Mazandaran Province of Iran)

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### Introduction

Several methods have been developed to aid in selecting a network of biodiversity protected areas. One of these methods is artificial intelligence which includes a number of different computer algorithms that use an objective function to find the best solution. An algorithm is a mathematical process or a set of rules used for problem solving. Recently, site selection algorithms have been widely used to identify areas of high conservation value. Two main types of site selection algorithms are optimal algorithms and heuristic ones. In this research, three types of heuristic algorithms, namely, annealing, greedy, and rarity simulated in the selection of the protected areas were compared to find the best regions for efficient environmental protection in Mazandaran Province. The effects of different parameters including conservation goals, scale, algorithms, and compactness of zones on the results were also investigated.

### Materials and methods

In this research, 26 forest cover types, the habitats of 8 mammal species, and prominent distribution area for 4 groups of birds were used as input criteria to select the candidate areas for environmental protection in Mazandaran Province. Multi-criteria evaluation method and Echelon analysis were used to model the mammals' habitats and the important bird distribution areas, respectively. Watersheds larger than 50 ha in size were defined and used for planning units in the process.

Simulated annealing, greedy, and rarity algorithms were used in the selection of best regions through Marxan software. Marxan delivers a decision support for reserve system design. The real strength of Marxan lies in its use of simulated annealing. However, Marxan is also capable of using such simpler, but more rapid methods, as greedy, rarity, and iterative improvement algorithms. The main aim of this research is the selection of a conservation network with minimum possible area so as to achieve all targets. The conservation target is to preserve minimum area of each forest cover type and the species habitat.

In the first scenario, the effect of different conservation targets including 30, 40, 50 and 60 percent of areal coverage of each protection criteria was investigated. In this scenario, Marxan was performed with 100 repeat runs, 10,000,000 iterations of simulated annealing and four different values of boundary length modifier (BLM) including 0,10,30,60 and 100. The BLM is used to control the level of fragmentation in the proposed conservation network, such that an increase in would result in a decrease of the network total boundary.

In the second scenario, the result of the simulated annealing was compared with the greedy and the best and average rarity algorithms. In this scenario, the target is 30 percent of each protection criteria with a BLM of 60.

In the third scenario, the effect of scale was considered in the six sub basins and the target is 30 percent of each protection criteria with a BLM of 60.

### Results and discussions

The results of the first scenario showed for all targets that an increase in BLM will increase the total area of the proposed conservation network and decrease its total perimeter. Moreover, the result for the best scenario showed for targets of 30, 40, 50, and 60 that 18.43, 23.95, 31.29, and 38.82 percent of the province is necessary

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for conservation, respectively. Selection of the best target is one of the preliminary steps in the selection of best protected areas network.

Figure 1 shows the graph of total reserve boundary length versus total area in the second scenario. According to this figure, the simulated annealing provides the best result in terms of area and perimeter. Using greedy algorithm, the total perimeter of the proposed conservation network was increased and the zones were much more dispersed. On the contrary, it can be understood from Figure 2 that the rarity algorithms produced compacter zones which have much larger area.

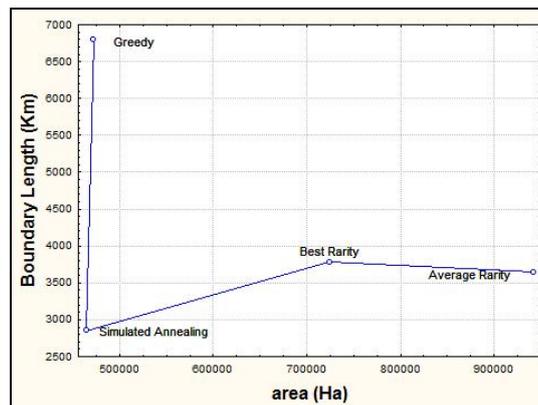


Figure 1. Total reserve boundary length versus total area

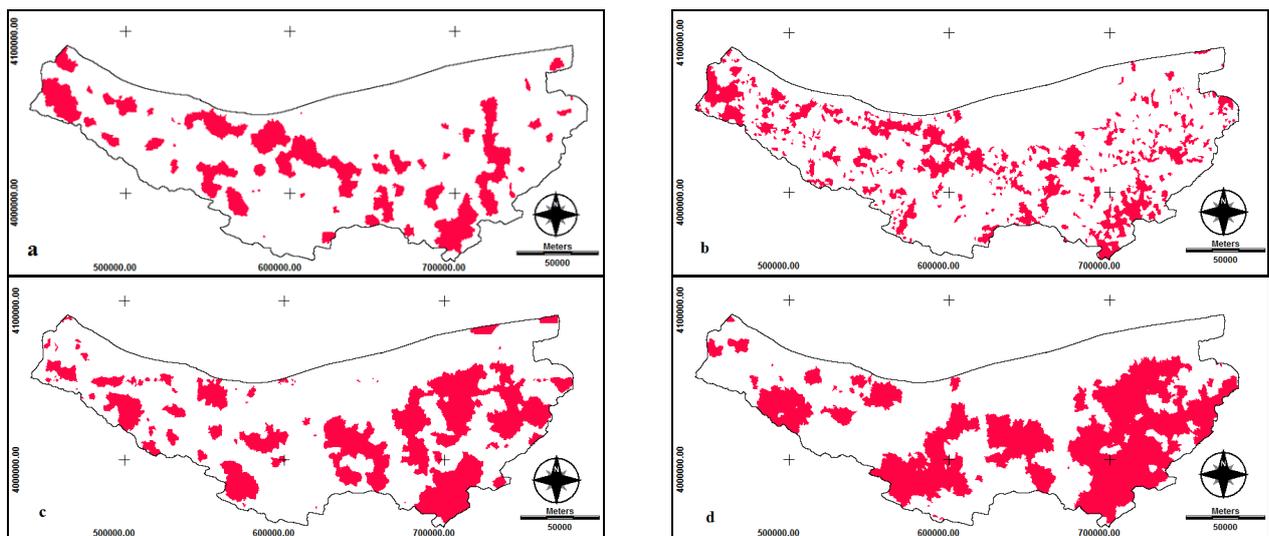


Figure 2. The proposed conservation networks by a) the simulated annealing, b) the greedy, c) the best rarity, and d) the average rarity algorithms. Data mapped in Marxan are with 30% conservation target, 100 repeat runs, 10,000,000 iterations, and four different values of BLM= 60.

Moreover, the time spent for the simulated annealing, the greedy, and the best and average rarity algorithms were 00:28:40, 1:49:43, 5:00:06 and 2:12:25, respectively. Implementation on a smaller scale and lower planning units reduced the time spent for the greedy and the rarity algorithms. The simulated annealing provided the best result in terms of area and perimeter.

The results of the third scenario showed that the sub basin-scale analysis identifies a larger area of high conservation value than that of the province-scale analysis. This was expected because all conservation targets needed to be met in each sub basin. The overlap between the proposed conservation network in the province-scale and sub basin-scale are 42.33 percent. This result showed that spatial scale impacts the distribution and number of zones which were considered high priority for conservation within an area.

In this research, irreplaceability analysis was performed on the proposed conservation networks generated by different algorithms. According to Leslie *et al.* (2003), we defined irreplaceability as the number of times a planning unit was included in the proposed conservation network out of 100 runs. For the simulated annealing, 7 planning units were chosen during every one of the 100 runs and were absolutely irreplaceable. Also, 29.84

percent of the planning units were never chosen during the 100 runs. For the greedy algorithm, 10 percent of the planning units were chosen during every one of the 100 runs and 76.65 percent of the planning units were never chosen. For the best and average rarity algorithms, 21.13 and 36.75 percent of the planning units were respectively chosen during every one of the 100 runs. For the average rarity algorithm, 63.19 percent of the planning units were also never chosen during the 100 runs. These results showed that the greedy and rarity algorithms produced many fewer different solutions in comparison to the simulated annealing.

According to Leslie et al. (2003), the efficiency of representation was defined as the number of those protection criteria with corresponding values close or equal to 1.0. This indicates that the proposed conservation network meets the conservation targets for the criteria. The results showed that, for the simulated annealing, the targets of the 29 to 32 criteria were met in the proposed conservation network. This value for the greedy algorithm was equal to 25 criteria. For the best and average rarity algorithms, 24 and 32 criteria were overrepresented in the proposed conservation network, respectively.

### **Conclusion**

The results of this study have shown that the conservation goals, scale, algorithms, and compactness of zones are influencing parameters on the selection of the best regions for efficient environmental protection. Consequently, determination of the appropriate values for these parameters is among the most important steps in conservation planning. The investigated parameters showed that the simulated annealing algorithm provides plausible results in all the cases and its application helps in the identification of best protection zones.

**Keywords:** greedy algorithm, Marxan, protected areas, rarity algorithm, simulated annealing.

## An Investigation on Cd Accumulation Potential in *Myrtus communis* and *Pinus brutia*

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### Introduction

Heavy metal contamination has disastrous effects on plant productivity and threatens human and animal health. Among metals, cadmium (Cd) is commonly released into the environment from industrial processes. Cd is known to cause cellular damage in plants by producing oxidative stress via the over-production of reactive oxygen species (ROS). To combat oxidative damage, plants have developed a defense system consisting of a variety of antioxidant enzymes which can neutralize, convert, and scavenge the ROS. Proline accumulates heavily in several plants under stress providing the plants protection against damage by the ROS. When translocated to the shoots, Cd causes strong oxidative stress and the inhibition of plant metabolism, including photosynthesis by direct and indirect mechanisms.

To reduce the environmental risks of cadmium contamination, phytoremediation has been considered as the most promising and a relative new method for cleanup of polluted environments. This study investigated Cd uptake by root through *Myrtus communis* and *Pinus brutia*. The objectives of this study were 1. to compare the Cd accumulation of *Myrtus communis* and *Pinus brutia* and 2. to provide evidence for the role of proline and soluble sugar in lead tolerance of the studied species.

### Materials and methods

Seeds of *Myrtus communis* and *Pinus brutia* sown into the pots with a diameter of 0.10 cm and a depth of 20 cm, each filled with 2 kg of soil. After germination, the samples of both plants were kept in greenhouse for two year. The plants of the same size were collected and used for the experiment. The experiment was done in triplicates by a random design. Cd in different concentrations of 0, 200, 500, and 1000 were made and poured in pots. After 70 days, the samples of roots and leaves were collected, washed and their proline, soluble sugar, and Cd accumulation were measured. Proline content was measured according to the previously described method by Bate (1973). Fresh seedlings (0.5 g) were ground in 3% (w/v) aqueous sulphosalicylic acid. The proline content was then estimated by ninhydrin reagent. The absorbance of the fraction with toluene aspired from the liquid phase was read at 520 nm. The proline concentration was determined by a calibration curve method that is expressed in mmol/g fresh weight. Soluble sugar content was measured according to the method described by Kochert (1978). Before the Cd analysis, the dried plant and soil sample were ground using a ball mill. The 2 g leaves and 1 g root and 2 g soil powder were digested with concentrated HNO<sup>3</sup>/HClO<sup>4</sup> solution for determination of the total Cd concentration. The Cd concentration was then determined using an atomic absorption novAA300.

### Results and discussion

The results presented in Table 1 show that proline was almost doubled when the Cd concentration increased to 500 ppm in *Pinus brutia*. A number of studies showed that proline can play an important protective role against heavy metal stress. It has been demonstrated that the free proline could chelate with the Cd ion in the plants and form a nontoxic Cd-proline complex. In contrast, increasing Cd concentration did not increase the proline

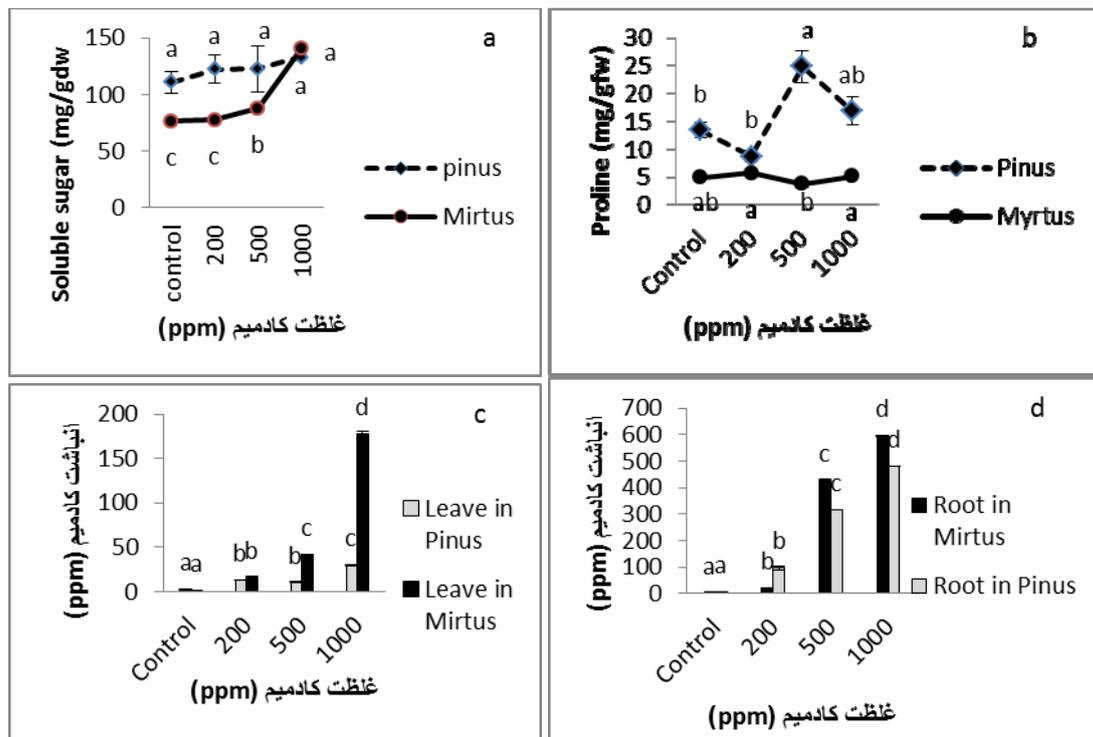
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content in the leaves of *Myrtus communis* as can be understood from Fig. 1. Thus, it could be suggested that the free proline might play an important protective role against the Cd stress and *Pinus brutia* had the stronger self-protection ability than *Myrtus communis*. Similar to the observations on *Myrtus communis*, the application of the Cd did not change the level of the free proline in the roots of *Solanum melongena*.

**Table 1. The effects of Cd on soluble sugar and proline, and accumulation amount in the roots and leaves of *Myrtus* and *Pinus*.**

Soluble sugar (mg/gdw)		Proline (mg/gfw)		Treatment (ppm)
<i>Myrtus communis</i>	<i>Pinus brutia</i>	<i>Myrtus communis</i>	<i>Pinus brutia</i>	
76 <sup>a</sup>	110 <sup>a</sup>	4.9 <sup>a</sup>	13.3 <sup>ab</sup>	Control
77.5 <sup>a</sup>	122 <sup>a</sup>	5.7 <sup>a</sup>	8.7 <sup>ab</sup>	200
87.9 <sup>a</sup>	122 <sup>a</sup>	3.7 <sup>a</sup>	24.8 <sup>b</sup>	500
140 <sup>a</sup>	132 <sup>a</sup>	5.1 <sup>a</sup>	16.8 <sup>b</sup>	1000
Accumulation in root (ppm)		Accumulation in leaves (ppm)		Treatment( ppm)
<i>Myrtus communis</i>	<i>Pinus brutia</i>	<i>Myrtus communis</i>	<i>Pinus brutia</i>	
0.4 <sup>a</sup>	3.3 <sup>a</sup>	0.4 <sup>a</sup>	2.1 <sup>a</sup>	Control
19.8 <sup>a</sup>	95.8 <sup>b</sup>	15.8 <sup>a</sup>	12.5 <sup>a</sup>	200
428 <sup>a</sup>	316 <sup>b</sup>	41 <sup>a</sup>	10.4 <sup>b</sup>	500
594 <sup>a</sup>	480 <sup>b</sup>	178 <sup>a</sup>	29.7 <sup>b</sup>	1000



**Figure 1. The effects of Cd concentration on the amounts of soluble sugar (a), proline (b), and accumulation amount in the leaves (c) and roots (d) of *Myrtus* and *Pinus*. Comparison within each plant.**

Soluble sugar was also doubled in *Myrtus communis* when the Cd concentration increased to 1000 ppm. In contrast, the soluble sugar did not change in *Pinus brutia* with an increase in the Cd concentration. Accumulation of the soluble sugar in response to heavy metal exposure seems to be seen in some plants. It is known that soluble sugar play an important role in osmotic adjustment in plants. Exposure to heavy metal, especially Cd, is known to deteriorate the plant water balance. With respect to the possible role of soluble sugar, the increase of

this solute may increase tolerance of the studied plants. The highest Cd accumulation in roots of *Pinus brutia* was equal to 480 ppm, of this only 29 ppm (6%) was transferred from the roots to the leaves. The highest Cd accumulation in the roots of *Myrtus communis* was equal to 593.9 ppm, of this only 177.97 ppm (30%) was transferred from the roots to the leaves. The results also showed that an increase in the Cd concentration in soil increased the Cd accumulation in the roots and leaves of the plants. It is important to note that of the total amount of ions associated with the roots, a part of it is only absorbed into the cells. A significant ion fraction is physically adsorbed at the extracellular negatively charged sites (COO<sup>-</sup>) of the root cell walls. The cell wall-bound fraction cannot be translocated to the shoots and, therefore, cannot be removed by harvesting shoot biomass through phytoextraction. Thus, it is possible for a plant exhibiting significant metal accumulation into the root to express a limited capacity for phytoextraction. Binding to the cell wall is not the only plant mechanism responsible for metal immobilization into the roots and the subsequent inhibition of ion translocation to the shoot. Metals can also be complexed and sequestered in cellular structures (e.g., vacuole), becoming unavailable for translocation to the shoot. Uptake of the metals into root cells is a step of major importance for the process of phytoextraction. However, for phytoextraction to occur, the metals must also be transported from the root to the shoot. Our result showed the Cd translocation in *Myrtus communis* is more than *Pinus brutia*. It is also concluded that for a high Cd accumulation in the leaves of *Myrtus communis*, this plant can introduce as a super accumulator and can use as a phytoextraction.

**Keywords:** cadmium, *Myrtus communis*, phytoremediation, *Pinus brutia*, proline

## Comparison of Carbon Sequestration of *Astragalus gossypinus* and *Dactylis glomerata* Species in Hezarjarib Mountainous Rangelands, Behshahr

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### Introduction

Nowadays climate changes as one of the major environmental issues have been put forward the most important challenge in sustainable development and poverty elimination. Carbon sequestration is a process in which carbon dioxide absorbs from the atmosphere and accumulates in carbohydrates form in plant tissues, litter, and soil. Rangelands ecosystems have a great potential in carbon sequestration because of including half of the lands on the earth. In addition, their carbon storage is about 10 percent of total biomass carbon storage in terrestrial ecosystems and 30 percent of organic carbon. In a global scale, about 500 billion tons of carbon sequester in the rangelands annually. To reduce atmospheric carbon dioxide and greenhouse gas balance, atmospheric carbon should be captured and sequestered. Carbon as one of the main greenhouse gases element sequesters by photosynthesis in plant biomass. Carbon sequestration by the rangelands plants is the most simple and the cheapest way to decrease this gas. Therefore identifying the species that have high ability to carbon sequestration can help us in the rangelands rehabilitation and reclamation.

### Materials and methods

The study area was 2598 ha including the enclosures and grazed rangelands in the mountainous region of Behshahr. This region is located on 53°54'01"- 53 52' 06" longitudes and 36° 38' 24"- 36° 36' 16" latitude. The maximum and minimum elevations are 1707 meters and 1043 meters above sea level, respectively. The area annual precipitation is 409 mm and the temperature is between -15 °C to 37 °C that its maximum occurs in the May. The climate is semi-arid cold based on Emberger technique. In this study, the effects of enclosure and grazed on the carbon sequestration was studied in two plant species in the Vezvar rangelands of Hezarjarib in Behshahr. Vegetation and soil sampling was done by random-systematic method with two 100 m transects and 40 plots. The plot numbers were obtained based on the plant distribution pattern in the area. The soil sampling was done in two depths of 0-15 and 15-30 cm with a total 80 soil samples.

Organic carbon determined by the Walkley-Black method. The species biomass measurement was done in above-ground and under-ground completely by weight and cutting method. Shooting and rooting organs of the species *Astragalus gossypinus* F. and *Dactylis glomerata* L. were separated from each other after transfer to the laboratory. The carbon sequestration coefficient of the plant organs was determined with combustion method. The carbon sequestration coefficient of the different species, organs, and the soils under these species were then analyzed in the Lab. In this study, Comparison of the carbon sequestration in two species was done by t-Test method. This investigation was done by SPSS v.19 and EXCEL software.

### Results and discussion

The statistical results presented in Table 1 showed that the mean of canopy percent in enclosure area is higher than that of the grazed region.

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Table 1. t-Test analysis of canopy percent in the enclosure and grazed area

Canopy percent	Study site	Mean	Std. deviation	Df	t
<i>Astragalus gossypinus</i>	exclosure	40.20	6.39	18	5.84**
	grazed	21	8.19		
<i>Dactylis glomerata</i>	exclosure	6.40	2.17	18	3.60**
	grazed	3.30	1.63		

\*\* Significant Level: 1%

The statistical results showed that the conversion coefficients of the plant biomass to the organic carbon in leaves, stems, and roots in non-grazed areas were more than that of the grazed areas. This increase in *Astragalus gossypinus* root (8.12%) and *Dactylis glomerata* stem (3.75%) had the most value (Table 2). Figure 1 show a significant difference between carbon sequestrations of various organs in both area .

Table 2. Ratio of biomass conversion to organic carbon in the enclosure and grazed area (%)

Species	Study site	Leaf	Stem	Root
<i>Astragalus gossypinus</i>	exclosure	5.45	5.34	8.12
	grazed	4.40	2.72	6.92
<i>Dactylis glomerata</i>	exclosure	2.71	3.75	2.36
	grazed	2.51	2.55	1.74

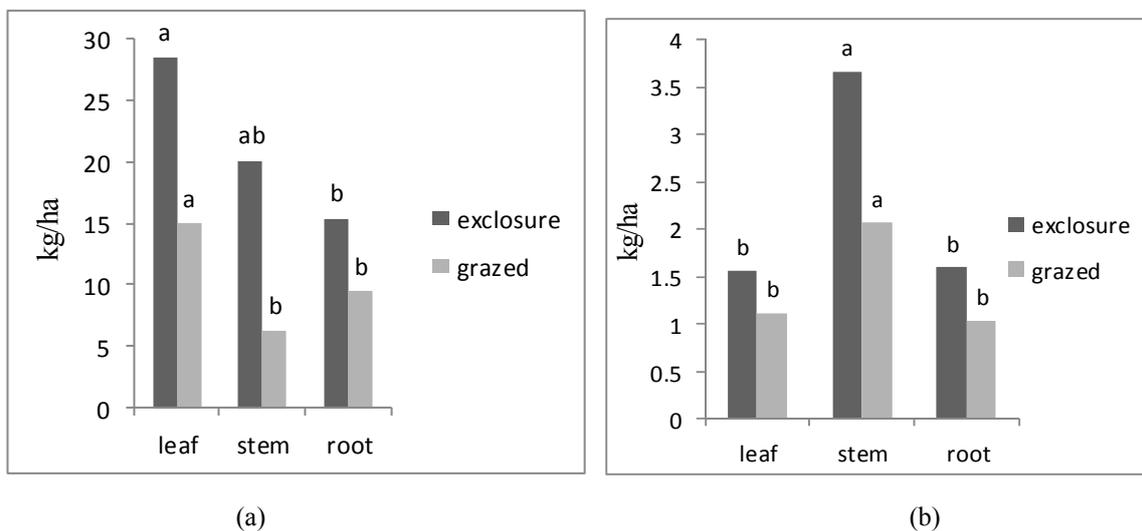


Figure 1. The mean carbon sequestration comparisons of *Astragalus gossypinus* (a) and *Dactylis glomerata* (b) in the enclosure and grazed area

Table 3 presents the results of total carbon sequestration in two studied sites. The total carbon sequestration by soil and vegetation in the non-grazed and grazed area showed no significant difference.

**Table 3. Total carbon sequestration of the soil and vegetation in the enclosure and grazed area**

Species	Study site	Mean	Std. deviation	Df	t
<i>Astragalus gossypinus</i>	<b>enclosure</b>	10364464.11	403085.93	18	0.325 <sup>ns</sup>
	grazed	9560630.7	343875.48		
<i>Dactylis glomerata</i>	<b>enclosure</b>	9959806.82	457485.10	18	0.919 <sup>ns</sup>
	grazed	8235804.23	378128.49		

Ns: Non-Significant

### Conclusion

The results show that the vegetation percent of *Astragalus gossypinus* and *Dactylis glomerata* in the enclosure areas was more than the grazed areas. The carbon sequestration of the species *Astragalus gossypinus* and *Dactylis glomerata* in enclosure site was more than the grazed site. These results confirm that grazing has a negative impact on carbon storage regardless of their vegetative form. Also, the data showed that the most conversion coefficients of *Astragalus gossypinus* and *Dactylis glomerata* is belong to the root and the stem, respectively. The high conversion coefficients of the root organs can say us the woody organs have high conversion coefficient to herbage organs due to high cellulose and lignin and low water. Comparison of the carbon sequestration potential in two studied sites showed no significant difference. This shows that the grazing has impalpable effect on the root biomass as a source of carbon input to the soil. Also the different organs have a difference in the carbon storage depending on the species type. So, the leaves in woody plant have a greater ability to carbon storage than grass plant form and the stem have more carbon than the other organs in the grass form. This showed that woody tissues have more ability for the carbon sequestration. The study of stored soil carbon also indicated that the soil has more carbon stored than plant species. This can be due to the other components that exist in the rangeland ecosystems such as animals, litter, and so on.

**Keywords:** carbon, rangeland, soil, pollution, grazing.

## Long-term Effects of Logging Damages on Quality of Residual Trees in the Asalem Nav Forest

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### Introduction

Chainsaw and cable skidder are two main logging machines for wood harvesting in the Caspian forests. Selection cutting is the main silvicultural method in these forests. Harvesting in the Caspian forests has the potential to damage the trees that are left standing. Damages to residual trees during the selection cutting operation may decrease the quality of residual trees and increase stand mortality through insect and disease infestation. The wounds can cause stem deformity and significant losses of the final crop volume and value. The wound characteristics such as size, location, and intensity are the main factors that influence on the future quality of damaged trees. Logging damages to the residual trees increase as the time passes. The literature review shows that minor damage to the stem of residual trees during logging operation can have a major impact on the final stand volume as future saw logs. In the Caspian forests, many studies focused on the primary logging damage (immediately after logging operation) and a few studies were done on the secondary logging damage (after years). The objective of this research was to study the condition of logging wounds on residual trees after 12 years elapsed in the Caspian forests.

### Materials and methods

The study was carried out in two adjacent compartments (35 and 42) of the district No., one of Nav watershed in Guilan province in the Caspian forest of Iran. The Nav watershed is located between 37° 38' 34" to 37° 42' 21" N and 48° 48' 44" to 48° 52' 30" E. The elevation of the study area is ranged from 1350 to 1600 m and the mean of annual precipitation and temperature are approximately 950 mm and 9.1°C, respectively. The original vegetation of this area is an uneven-aged mixed forest and is dominantly covered by *Fagus orientalis* and *Carpinus betulus* stands. These compartments selectively logged by ground-based logging operation during December and January of 2000. The characteristics of wounds (size, intensity, and location) on the residual trees were measured immediately after logging operation. The condition of wounds was restudied after 12 years from logging operation in the year of 2012.

### Results and discussion

The results of this study showed that 67.1% of wounds were closed and 32.8% of the damaged trees were not able to improve their wounds. About 4.2 percent of wounds caused to tree mortality as shown in Table 1.

Table 1. The condition of wounds after 12 years from logging damage in the study area

Frequency	Condition of wounds			
	Closed	Open	Decayed	Tree destroyed
Number	194	52	31	12
Percentage	67.1	18.0	10.7	4.2

Table 2 shows the condition of wounds on the trees with different diameters at breast height (dbh). The trees of dbh < 40 cm are more sensitive to logging wounds so that 58.4% of damaged trees of dbh < 20 cm and 10.5% of damaged trees with a dbh of 21-40 cm caused to tree mortality.

Table 2. The condition of wounds on the trees with different diameter at breast height (dbh)

Tree dbh (cm)	Wound condition							
	Closed		Open		Decayed		Tree destroyed	
	N	%	N	%	N	%	N	%
< 20	1	8.3	1	8.3	3	25.0	7	58.4
21 - 40	34	89.5	0	0	0	0	4	10.5
41 - 60	89	92.7	4	4.1	2	2.1	1	1.0
61 - 80	49	70.0	13	18.6	8	11.4	0	0
>81	21	28.7	34	46.6	18	24.7	0	0

The effect of wound characteristics (size, intensity and location) on its future condition was studied and the results were shown in Table 3. Our study indicated that the wounds near the ground have a greater incidence of decay compared to the higher wounds. The wound size is one of the most important characteristics related to decay. The results showed the wounds in sizes <25 cm<sup>2</sup> had the most ability of healing. The bark squeezed intensity of bole wounds didn't caused to tree mortality; while about 8.3% of wood-damaged intensity of bole wounds caused to tree mortality and 19.8 % of them caused to wood decayed (Table 3). Overall, results of this study indicated any major wound located in the lower section of the tree have the potential to greatly reduce the quantity and quality of the future wood product by causing stain or decay in the high-value butt log.

Table 3. The condition of wounds in the different wound characteristics

Wound characteristics	Wound condition							
	Closed		Open		Decayed		Tree destroyed	
	N	%	N	%	N	%	N	%
<b>Size</b>								
< 25	116	90.6	9	7.0	3	2.4	0	0
26-100	74	70.5	29	27.6	2	1.9	0	0
101-1000	4	11.8	12	35.3	15	44.1	3	8.8
>1001	0	0	2	9.1	11	50.0	9	40.9
<b>Intensity</b>								
Bark squeezed	60	88.2	8	11.8	0	0	0	0
Bark removed	79	79.0	12	12.0	7	7.0	2	2.0
Wood damaged	55	45.5	32	24.6	24	19.8	10	8.3
<b>Location</b>								
Root	4	19.1	10	47.6	5	23.8	2	9.5
<1 m	73	60.4	20	16.5	20	16.5	8	6.6
1 - 2 m	53	69.8	19	25.0	3	3.9	1	1.3
>2 m	64	90.2	2	2.8	4	5.6	1	1.4

Table 4 presents the results of Chi square test for the effect of tree dbh and wound characteristics on the wounds condition. These results showed that the dbh of trees and wound characteristics (size, intensity, and location) have significant effect on wounds condition (Table 4).

Table 4. The results of Chi square test for the effect of tree dbh and wound characteristics on the wounds condition

Factor	Df	Chi Square Value	P-Value
Tree dbh	12	208.3	0.00**
Wound size	9	227.6	0.00**
Wound intensity	6	52.9	0.00**
Wound location	9	50.2	0.00**

\*\* Significant at  $\alpha = 0.05$ .

### Conclusion

The results of this study showed that logging damage to stand can be reduced substantially. To achieve sustainable forest management, the main requirements are minimization of the logging damages. In the context of selection cutting management, minimizing logging damage to residual trees must therefore remain a major

objective. In order to minimize felling damage, directional felling must be applied considering the skid trails. Pre-harvest planning and identifying the winching area before logging operation can reduce damage to the stand in the Caspian forests.

**Keywords:** logging damage, selection method, residual stand, bole injury, Nav forest.

## The Application of GIS in Site Selection and Space-Place Analysis of Pollution and Air Pollutant Sources in Metropolitan Kermanshah

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### Introduction

The process of urbanism in countries that are developing, like Islamic Republic of Iran with increasing in the number and the size of cities and the fast population admission have caused problems including in-official economics and in-official settlement led to high population concentration in main and old places of city and increase in air pollution in cities (Pazhouhian and MoradHasel, 1386). The most atmospheric pollution of the big cities of Iran has direct relation with the kind and the rate of the pollutants in crowded places and full of population.

In this study, we have used density classification method for studying relation between population and quantity and kind of atmospheric pollution in the big city of Kermanshah based on estimating number of people and calculating pollution in statistical blocks including 62 statistical point samples with determining rate of quantity of populations and geographic position of the study area by using Global Positioning System (GPS). Statistical populations of this research are including quantity of populations and quantity and kind of pollution in 7 days time period in the suburb of Kermanshah City.

Using Geographical Information System (GIS) has high advantage as a main tool for geographic analysis to recognize existing law in relation between human and environment. Using GIS in study and analysis of space-place distribution of pollutant area with quantity and kind of air pollutions was started in 1970. This will be possible to provide the place station data, order and spatial pollution data, assimilation data and spatial analysis by the facilities and technique of this system. Preparing place data station about parameters including kind of pollutants, determining geographical coordinate workshop, factories and busy population place, quantity of air pollution and usable managing possibility for interring, saving, updating and taking data with speed and high quality are main ability of geographical information system technology (GIS central of Tehran municipality, 1384).

Geographical information system with the decision support system (MCDM) can be used effectively in scanning and managing of atmospheric pollutions data for studying place distribution of differential pollutants and evaluations trend rate of pollutant quantity as an environmental decision support system (EDSS). The EDSS is useful in controlling and intelligent managing of critical pollution in the big cities specially Kermanshah.

Cheraghi in a research entitled "studying comparing of air quality in Tehran and Isfahan cites offer ways to improve" topic of working in 1387. He concluded that the most pollution is recorded in June, September, October, and January for Tehran and also in June for Isfahan. Furthermore, this study shows that 60 percent of the days have been above standard index. Ardakani & Cheraghi in research with "sanitary quality evaluation about the air of Tehran with air quality index to measure station of air pollution separately" showed that air quality of Tehran city has been increased above standard limit according to EPA for 261 days in 1385. Mousavi, in a study entitled A Comparative study of air quality in Tehran since 1997 to 1998 concluded in 1997 that air quality in 32 percent of the days have been insanitary and 5 percent of the days have been very insanitary.

### Discussion

United States Environmental Protection Agency EPA selected 6 main pollutions as criteria and divided to 2 primary and secondary categories. Primary pollutions are substances that inter directly from sources into the ambient air including five pollutants that are carbon monoxide (CO), nitrogen dioxide (NO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), particulate matter with diameter less than 10 microns (PM-10) and lead (pb). Secondary pollutants refer to material that produced by interactions in the air surrounding ground and in this category is ozone (O<sub>3</sub>).

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### **The air pollution index**

One of the most widely used index for reporting and comparing the air pollutant is PSI index (Pollutant Standard Index) that has been developed by the Environmental Protection Agency of America (ESI). The index is calculated based on measuring concentrations of five major air pollutants (CO, PM<sub>10</sub>, O<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub>) and it is possible to convert PSI index.

### **Data used**

Materials and tools have been used in the research include:

1. Maps of (a population density map with scale 1: 25000, highways and streets maps, prevailing wind direction maps, preparing DEM), to determine geographical position of the urban place of study area (statistical samples) by GIS
2. The software used includes: Microsoft Office Excel, Arcview, GIS and lateral Software as Crime Analysis and Case
3. Statistical data and population data

Process of this study involves the following steps:

First stage: library review for previous researches, characteristics of pollutants, and the evaluating of layers for GIS.

Second stage: collecting and entering data, positions, elevation points, extra separately in Excel software (Excel) with dbf format that have been stored in separated columns.

Third stage: calling data and statistical tables on the Case and Crime Analysis software

Fourth stage: determining positioning points of air pollution measuring stations, recognizing major pollutant point of city, direction and kind of pollutants distribution are in the city surface based on the kind of pollutant scene of height and density of pollutant, determining air pollutant index as kind and quality of air in emergencies and crises time to (digital layers) format in the Arc GIS software.

Step five: preparing of digital maps and graded class of the effected parameters in the production and distribution of pollutants.

### **Materials and methods**

The research is based on density classification method on bill of population amount and pollutants measuring on the statistical blocks that included 62 statistical point samples with geographical places by GPS for studying the relation between population to amount and kind of pollutants in the big city of Kermanshah. Statistical population in this research is population data, pollution quality, and kind of pollution that are collected for a period of 7 days in Kermanshah. The basic tests that used are median center tests, distance from standard deviation and ellipse of standard deviation. Near neighbor index has been used for identifying the quantity of air pollution between clustering tests. GIS and GPS and pollutant measuring tools and Case & Crime Analysis software it is possible to recognize the place of pollutants in the city.

### **Statistical methods of basic graphic**

The first group of place analysis method is basic graphic statistical methods that by quality attention to center and space distribution of pollutants recognize the geographical suburb of the city. Standard deviation Ellipse and median center points are comprehensive statistical tests. Median center point can be used as an approximate index for comparing of space distribution of pollutants place or study about kind of specific pollutants in the time periods.

In other word, the median center has been determined in central location to basic average of all forms of contaminated sites. Standard deviation Ellipse has been showed in dispersion levels of the places of air pollution.

### **Median center and standard deviation ellipses**

The median center of the polluted sites (air pollution) is based on five major air pollutants (CO, PM<sub>10</sub>, O<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub>) of Kermanshah city that are located on Azadi Square, across the Shahid Beheshti Boulevard from the 22 Bahman Crossroad to Sepah Square, Modaress Crossroad to Aiatollah Kashani Square, Shahid Ashke Talkh Street to end of Jalili Street, the suburb of Azadegan Square. Ellipse standard deviation shows pollutants distributional area of Kermanshah that has a stretch from north to south.

### **Kernel density estimates test**

Kernel density estimate test is one of suitable methods for drawing statistical data and analytical-definitions as the smooth surface in the geographic areas. Kernel density estimates test make smooth surface of data density changes as amount and kind of pollutants in the site. This calculation was done by Arc GIS software based on mentioned methods.

Analytical method for Kernel test is another way for space analysis of air pollutant in cities. In this method, relation between quantity and kinds of pollutants to density of population is measured in geographic units with specified dimensions.

### Conclusions

Results show that the emission of 5 atmospheric pollutants follow clustered patterns in Kermanshah. Geographical distribution average center of air pollutant point are coordinate toward city center (Nawab three ways to Kashani Square). Ellipse standard deviation of the pollution has been stretched in the North West, and South East. Closer look at the standard ellipse of distribution is showing more stretch directed toward South East. The nearest neighbor index of statistical test has been used to determine the random distribution or clustering of Atmospheric pollutants emission in prepared research. Quantity of the nearest neighbor index in the distribution of pollutant points is equal.

**Table 1. The amount and kind of atmospheric pollution in the city of Kermanshah**

O <sub>3</sub> (ppm)	CO <sub>2</sub> (ppm)	NO <sub>2</sub> (ppm)	NOX (ppm)	SO <sub>2</sub> (ppm)	PM <sub>10</sub> (µg/m <sup>3</sup> )	Kind of air pollutant
73.91	7.79	138	136	56.58	89.85	Quantity of air pollutant

Source: the authors

The distribution quantity of atmospheric pollution with 5 pollutants (CO, PM<sub>10</sub>, O<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub>), from insufficient fuels of petrochemical industries have clusterly distribution with the statistical form. Because when the result of the nearest neighbor index test was smaller than that showed measured information has cluster pattern in polluted place of city.

In addition, Kernel density method that's more suitable for drawing geographical statistical data, particularly on time and location, was used to determine and analyze characterizes of 5 pollutants (CO, PM<sub>10</sub>, O<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub>) as the amount and direction of distribution in the Kermanshah. It was determined based on this method that major concentrated atmospheric pollutants are resulted from fossil fuel of cars in Azadi Square, across the Shahid Beheshti Boulevard from the 22 Bahman Crossroad to Sepah Square, Modarres Crossroad to Aiatollah Kashani Square, Shahid Ashke Talkh Street to end of Jalili Street, Suburb of Azadegan Square. Main centers of 2 inferior places are located in Moalem and Elahieh, small towns in Kermanshah.

**Keywords:** environmental pollution, Geographic Information Systems (GIS), Kermanshah, space-place Analysis.

## An Investigation on the Status of Troposphere NO<sub>2</sub> Over Iran During 2004 to 2012

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### Introduction

NO<sub>2</sub> is not only a potential air pollutant in urban and industrial environments but also a precursor for smog of urban environment that is another ozone pollutant as well. Some of the urban environments in Iran have high tropospheric and near surface NO<sub>2</sub> which requires research attentions especially in these years. That is the issue of concern in the present study using satellite data of OMI from 2004 to 2012. Here, we compare the trends of NO<sub>2</sub> for some cities of Iran while looking at the correlation between the near surface values of NO<sub>2</sub> and that of the tropospheric column values.

### Material and methods

Spatial and temporal variations of the tropospheric column nitrogen dioxide over Iran are studied using the satellite data of OMI from 2004 to 2012. The surface data of NO<sub>2</sub> for Tehran is also considered. The data were acquired from the air monitoring stations of the city for this period. Weather synoptic maps were also used for interpretation of the observed NO<sub>2</sub> variations. The monthly mean values of NO<sub>2</sub> for large cities were plotted for comparison; while long term trends for all this period were also presented for the large cities as well as the other less populated places for comparison. The maps of overall variations of column NO<sub>2</sub> for the Middle East were also obtained from the TEMIS database that have its monthly mean values as maps as well as the data for all places over the globe.

The synoptic maps were also obtained from the NOAA web site. This web site has the weather maps for different pressure levels of the globe, for various parameters of meteorology. Although, we only used the maps of 500 mb for the Middle East for the cold season months, as December. As will be observed, the higher values of NO<sub>2</sub> are found in colder months.

### Results and discussions

Typical monthly averages of NO<sub>2</sub> for large cities of Iran for 2010 show that depending on the size of the city the monthly average of NO<sub>2</sub> increases with city size. This is particularly so for cold months due to larger tropospheric column NO<sub>2</sub>. Figure 1 compares the mean monthly values of NO<sub>2</sub> of tropospheric column with its near surface values for some of the locations in Iran for winter months. It shows a good correlation between these two for nominal winter months. Such a correlation can be used to estimate the surface NO<sub>2</sub> from that of tropospheric column NO<sub>2</sub> measured by satellite. Larger values of NO<sub>2</sub> for winter months can be due to a lower temperature as well as a less sun shine that affect the NO<sub>2</sub> concentration in the photochemical smog processes over large city environments with large traffics. The long term trends for all large cities are on the rise, as an example Figure 2 shows such a trend for Tehran. The near surface NO<sub>2</sub> over Tehran also show that its concentration is the highest in the northern part of the city. This is mainly due to the anabatic winds due to mountain circulation that can transport air pollutants as NO<sub>2</sub> to the northern parts of Tehran. The valleys in the northern parts of the city from west to east also appears to have substantial concentrations of NO<sub>2</sub> indicating that up-valley winds may suck the polluted air from the urban environment. This process requires further monitoring of near surface circulations.

It is interesting that after a rain of substantial amount (typically larger than 10 mm), sometime (a couple of days) all the pollutants increase and reach the early levels except ozone related to photochemical smog in which NO<sub>2</sub> also have some contributions and increases very shortly after the rain period.

Results show that the maximum values of the tropospheric NO<sub>2</sub> occurs in the cold months including

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Novembers and Decembers with a typical value of  $23.28 \times 10^{15}$  molec/cm<sup>2</sup>; while its minimum occurs in summer (July) with a typical value of  $5.06 \times 10^{15}$  molec/cm<sup>2</sup>, with an annual mean of  $8.7 \times 10^{15}$  molec/cm<sup>2</sup>.

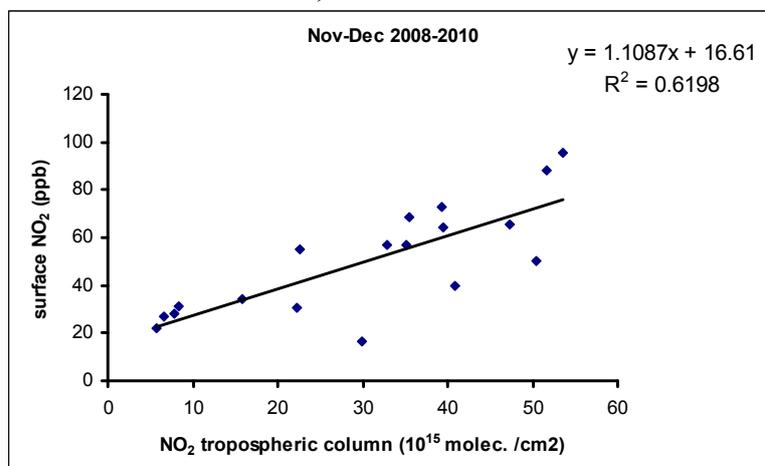


Figure 1. Linear correlation between surface NO<sub>2</sub> and the tropospheric column NO<sub>2</sub> for some Iranian locations for November and December 2008-2010

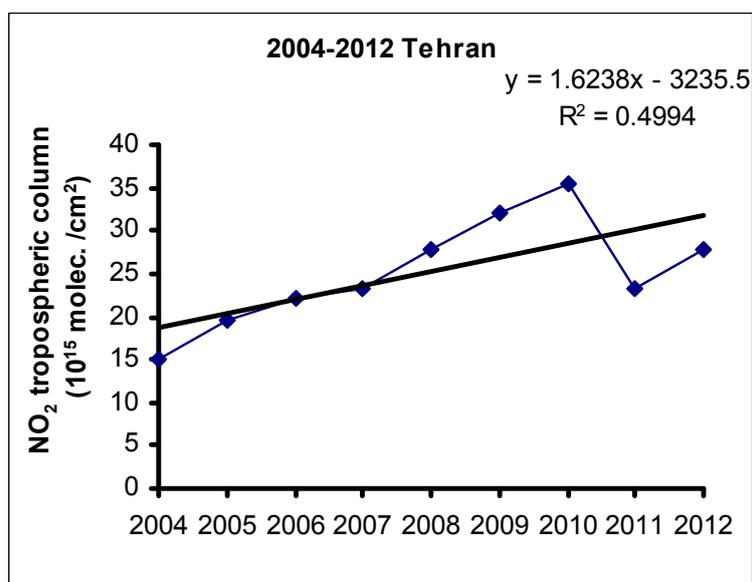


Figure 2. Long term trends of monthly mean tropospheric column NO<sub>2</sub> for September for the Geophysics station of Tehran during 2004 and 2012

Table 1 shows the average values of NO<sub>2</sub> for some of the large cities of Iran indicating that as the cities get larger the concentrations of NO<sub>2</sub> consequently increase. Tehran as the largest city has the largest values of NO<sub>2</sub>.

Table 1. Nine year averages of tropospheric NO<sub>2</sub> for December for some large cities of Iran (10<sup>15</sup> molec/cm<sup>2</sup>)

station	Tajrish	Shahin shahr	Mashhad	Rasht	Marv dasht	Tabriz	Ahvaz
state	Tehran	Esfahan	Khorasan	Gilan	Fars	Azarbayejan	Khoozestan
NO <sub>2</sub>	40.29	22.18	9.66	9.29	8.31	6.42	6.03

The synoptic patterns associated with larger concentrations of NO<sub>2</sub> in cold months show a strong ridge over the area in the middle troposphere. During these months, we have observed stronger near surface inversion based on the temperature data on the surface tower. The wind speed for these periods seems to be very low enhancing

the levels of air pollutants especially the NO<sub>2</sub>. Under such conditions, local circulations play a major role in advection of near surface pollutants towards some areas as for example towards the northern area of Tehran increasing the NO<sub>2</sub> to very large values that was also observed in the satellite data.

### Conclusion

The monthly mean values of the tropospheric column NO<sub>2</sub> for the large cities of Iran show that its maximum occurred in the cold months; while the minimums were found for the summer months. The spatial concentrations of NO<sub>2</sub> over the area show larger values for large cities in proportion to the size of the cities with the largest concentration for Tehran. The trends of its concentrations for this area show that it is on increase for the large cities as Tehran, Esfahan, and Shiraz with no particular trends for the other places in this area. Also near surface values of the NO<sub>2</sub> for Tehran show that the northeastern part of the city has the largest concentrations indicating that the southeasterly anabatic wind that advects the pollutant towards this area may be responsible for this finding. The synoptic condition associated with high tropospheric column NO<sub>2</sub> concentration is the existence of a high pressure upper air ridge with low near surface winds and stronger stability. Often the near surface value of the NO<sub>2</sub> and the tropospheric column value have the same behavior. They show a good correlation which can be used to estimate the surface values from that of the satellite measurements.

**Keywords:** Iran, meteorological conditions, surface sources, tropospheric nitrogen dioxide.

## Optimization of DRASTIC and SINTACS Models According to Geographical Information System with the Use of Analytical Hierarchy Process (AHP) (Case Study: Andimeshk Plain)

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### Introduction

Because of expansion of agricultural activities, of excessive use of chemical fertilizers, and of location of the municipal and industrial wastewater of Andimeshk, it is possible for this aquifer to be polluted. Therefore, the aim of the present study is to assess the aquifer vulnerability of Andimeshk plain and to recognize the sensitive areas against pollution. This work can be conducted using the DRASTIC and SINTACS models. Although, these models are among the most used models for the assessment of aquifer vulnerability, these models should be corrected on the basis of local hydrological conditions to obtain correct results. Therefore, the main aim of this study is correction of the DRASTIC and SINTACS models according to the local hydrological conditions and finally determining the best aquifer vulnerable model for the plain.

### Materials and methods

#### Study area

The Andimeshk plain is located in the north west of Khuzestan province with an area of 295 km<sup>2</sup> and its geographical coordinates is in north latitude, 32° 15' to 32° 35' and east longitude 48° 29' to 48° XX'.

#### DRASTIC and SINTACS models

Generally, parameters used in these models consist of depth to water table, net recharge (effective infiltration), aquifer media (aquifer hydrogeologic characteristics), soil media, topography (slope), impact of vadose zone (unsaturated condition), and hydraulic conductivity.

#### Analytical Hierarchy Process (AHP)

The AHP method is based upon the construction of some series of Pair-Wise comparison matrices (PCMs) which compare all the criteria to one other. Saaty (1980) suggests a scale of 1-9 for the PCM elements, wherein the value of 1 suggests that the criteria are equally important and the value of 9 shows that the priority of this one is extremely more than the other one in this comparison.

#### Data acquisition

Based on the collected data and required information, a database in the GIS environment was prepared for calculation of final vulnerability index in the methods. So the ArcGIS9.3 software has been used. The main aim of the criteria maps preparation is its modulation using overlaying technique and finally after that the preparation of aquifer vulnerability maps by the models. Finally to identify the accuracy of specific weights for parameters, the models have been analyzed according to their sensitivity to the real conditions. In the present research, the entered parameters according to the DRASTIC and SINTACS model theories the corrected weights by the AHP method for the preparation of maps indices were used as well. To determine the optimized weight of each parameter, the correlation coefficient calculated vulnerability indices by the methods and nitrate concentration have been calculated using Simple Linear Regression Analysis (SLRA). Finally according to a high correlation

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coefficient of each index with the nitrate concentration, the optimized model has been determined for the assessment of aquifer vulnerability. It is necessary to mention that for reduction of decision making errors and correct choice of the weight, many expert views were used. Therefore, many models were executed for the calculation of the aquifer vulnerability index.

### Sensitivity analysis

In the present research single parameter analysis method has been used to analyze the sensitivity of used models.

### Specific vulnerability to nitrate pollution

The Composite DRASTIC index (CD index) is an adaptation of the DRASTIC index based on the addition of a new parameter defining the potential risk associated with land use (L). The risk potential map related to land use using the same methodology applied for other parameters of DRASTIC index will be prepared. It is necessary to mention that calculation of specific vulnerability of SINTACS method was performed according to the same methodology used in the Composite DRASTIC index calculation (Composite SINTACS index or CS index). To prepare specific aquifer vulnerability map of the plain using the DRASTICS and SINTACS models at the first step because of the importance of parameters of this area in the transfer of pollution into the aquifer. These parameters with the weight of 5 will be added to both parameters in a normal way. For correction of the weight given to this parameter in the real condition using Simple Linear Regression Analysis (SLRA), the correlation of specific vulnerability indices has been determined using both aquifer models and the Nitrate concentration. In this type of vulnerability also the method of weighting based on the AHP method has been used for determination of optimized weight according to the real condition of the area.

### Results and discussion

The results obtained from overlaying of criteria maps of the DRASTIC and SINTACS models show that the final intrinsic vulnerability index for the DRASTIC model is between 73 and 157 and for the SINTACS model is between 90 and 171. To check the accuracy of specific weight of both model parameters, the single parameter sensitivity analysis has been done based on local condition. The statistical results obtained from the single parameter sensitivity analysis of the models show that the most effective parameter in the calculation of intrinsic vulnerability of the studied aquifer is the unsaturated area parameter (with the average effective weight of 28.59 and 29.32 percent respectively) and topography (with average effective weight of 8.83 and 7.04 percent respectively) have the minimum effect in the calculation of this index. Comparison of the effective and theoretical weights for the DRASTIC and SINTACS parameters models are not fully matched with each other. Considering this inconsistency, the parameter weights for both models have been corrected by the AHP method according to hydrological conditions. The results obtained from this method show that among the models executed for the DRASTIC model, the best correlation coefficient is 0.752, and it has been chosen as the optimized model; because it has better correlation coefficient compared to the normal DRASTIC (0.741). The SINTACS model has been determined as the optimal one after determining the correlation coefficient in different corrected SINTACS models and finding that the greatest correlation coefficient was 0.659 due to having a greater correlation coefficient against the normal SINTACS model (0.636). Finally between two determined optimized model, the corrected DRASTIC model has been determined which is because of having more correlation with the Nitrate concentration as the optimized model for the assessment of final aquifer intrinsic vulnerability of Andimeshk plain. The results obtained from Simple Linear Regression Analysis (SLRA) between CD and CS indices with aquifer Nitrate concentration show that the correlation coefficients for both of the indices are 0.651 and 0.529, respectively. After execution of different models by the AHP weighting method and determination of their correlation coefficients with the Nitrate concentration, the best model of specific aquifer vulnerability model for the plain have been determined according to the most correlation coefficient for both of the methods. Specific vulnerability map obtained from the corrected CD index has been used for the evaluation of the possibility for the studied aquifer, because of its greater correlation coefficient (0.749 and 0.657 respectively for CD and CS indices). Generally, the optimized weight of the composite DRASTIC and DRASTIC model according to hydrological condition of the Andimeshk plain has been presented in Table 1.

**Table 1. The optimized weights of the DRASTIC and Composite DRASTIC model parameters**

Parameter	Primary weight	Optimized weight	
		DRASTIC	Composite DRASTIC
Depth to watertable	5	3.86	3.93
Net recharge	4	2.03	2.28
Aquifer media	3	1.22	1.35
Soil media	2	2.55	2.84
Topography	1	1	1
Impact of vadose zone	5	5	5
Hydraulic conductivity	3	1.59	1.72
Land use	5	—	1.1
Inconsistency Rate	—	0.035	0.052

### Conclusions

Increasing the correlation coefficient of the optimized DRASTIC, SINTACS indices, and the corrected CD and CS indices by the AHP method with the nitrate concentration of the studied aquifer show that optimization of the vulnerability models according to the hydrological condition of the area is more compatible with the aquifer real conditions. The vulnerability index of the corrected DRASTIC model is between 51.81 and 122.69. According to the obtained results from the corrected CD index, the specific vulnerability index for the studied aquifer is between 65.83 and 135.85. Although the nitrate pollution's risk for the Andimeshk plain is not evaluated as a high value, a crucial environmental management should be conducted in this area due to this area's condition, urbanization growth, agricultural development, and increasing disposal of municipal, industrial, and agricultural wastewater. This is also possible by cooperation of society members, experts, and authorities and by correcting of land use planning.

**Keywords:** analytical hierarchy process (AHP), Andimeshk plain, DRASTIC, SINTACS, vulnerability.

## A Feasibility Study on Qualitative Indicators in Isfahan City

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### Introduction

Quality of urban life is known as one of the major elements of urban development. Thus, evaluation urban environmental quality has much importance in the planning of urban development. Cities are complex ecosystems affected by social, economic, environmental, and cultural factors. Inefficient urban planning and management and lack of coherent environmental policies have led to many urban environmental problems in a lot of modern cities. The number and scope of these problems are significant and they are becoming serious threats to the health and safety of residents.

Environmental damages in large cities of Iran such as Isfahan have threatened health and welfare of the residents. Therefore, evaluation of environmental elements quality in Isfahan city for identifying the current state of environment is necessary. Thus, the main objective of this study is to measure qualitative indicators in different fields using urban environmental quality evaluation model in Isfahan city.

Recent experiences for providing the analytical methods in urban environmental quality evaluation have shown the worth of indicators.

Therefore various collections of indicators have designed for evaluation of urban environmental quality. The Foundation's work on urban sustainability indicators started in 1994 when some researchers proposed a set of indicators based upon the charter of European sustainable cities and towns. The framework was subsequently tested by the cities participating in the research network of medium-sized cities. In another research, the Sustainable Society Index (SSI) has been developed for use in 135 different countries. The SSI integrates the most important aspects of sustainability and quality of life of a national society in a simple and transparent way. In another research, urban sustainability is evaluated by 19 indicators in four cities in China. Although, all four cities are moving towards sustainable development, the current situation shows still weak sustainability in three cities and even non-sustainability in one. Researchers in Italy used the Dashboard of Sustainability to measure the local urban sustainable development. 61 various indicators has presented in their work. The Dashboard of Sustainability (DS) is a mathematical and graphical tool designed to integrate the complex influences of sustainability and to support the decision-making process by creating concise evaluations. In a similar study, 51 sustainability indicators have selected for evaluation of the urban characteristic of Taipei city. These indicators are classified into economic, social, environmental, and institutional dimensions. Analysis of the results demonstrates that social and environmental indicators are moving towards sustainability indicators, while economical and institutional dimensions are performing poorly. Some of the best foresaid have been used appropriately in order to evaluate urban environment in Isfahan. Iran has recently paid special attention to evaluate the urban environmental quality by the use of various indicators too. In a main study, after reviewing traditional methods, a model has been presented for evaluation of urban environmental quality. On the other hand, quantitative and qualitative characteristics of Tehran's environmental quality were evaluated as average with a score of 53.3% in a similar study that was conducted in 1996. After that, Tehran's urban environmental quality has been evaluated again by reforming and optimization of previous indicators.

In this study, application of urban environmental quality evaluation model had been tested based on various urban quality models and indicators in Iran and the world. The recent model and indicators along with some modifications had been adopted for use in the evaluation of Isfahan city.

### Materials and methods

The case study is 14 urban districts in Isfahan city with an expansion of 482 kilometers and a population of 1.7 million people.

In the present study the various kinds of patterns and models of sustainability indicators have been studied for evaluating the quality of urban environment of Isfahan. Also, urban environmental quality evaluation model and its application which had been tested in evaluating the quality of Tehran's urban environment have been compared. Then, the final collection of indicators for evaluating the quality of urban environment in Isfahan had been collected, with comparative analysis of the mentioned studies and the various indicators of international researches.

In the first step, the various indicators of different countries have been extracted. In the next step, the similar indicators with Iran's indicators have been removed. Thus, in the following stages the mentioned indicators were adjusted based on the current information. Finally, a collection of 11 indicators and 53 measures have been chosen and categorized in the form of the adjusted model of the previous studies. The model with a simple mathematical order, determines the quality of urban environment to the language of numbers based on compared common criteria. The model contains four layers and the main indicator is at the first. There are sub indicators in the second layer. It was divided to elements. Finally, the third layer consists of the measures. As it is observed, the measures are the smaller form of the indicators of the higher layers which can be measured. For evaluation, the information has been collected from various studies such as Isfahan city statistic yearbook and other organizations.

## Results

Table 1 has shown the quality of urban environment for the 11 main indicators.

**Table 1. Eleven main indicators of Isfahan's environmental quality**

Main indicators	score	Condition
Natural environment	73%	Desirable quality
Individual health & treatment	93%	very desirable
Safety & security	40%	Middle ranking quality
Social environment	43%	Middle ranking quality
Education	85%	very desirable
Economy & employment	66%	Desirable quality
Service centers distribution	75%	Desirable quality
Urban facilities	91%	very desirable
Transportation	81%	very desirable
Housing	58%	Middle ranking quality
Culture, Art, Recreation	%63	Desirable quality

In the natural environmental indicator, the city's desirable quality was due to air pollution, daily water use per capita, number of regular water outage, permanent or seasonal status in the Zayandeh Rud river, quality of soil, soil pollutant, average annual rainfall, average temperature with scores of 83%, 75%, 100%, 50%, 50%, 100%, 0%, and 50%, respectively. In fact the main problem in this section is related to the undesirable quality of average annual rainfall. Also, though the desirable quality of air pollution, high density of  $Pm_{10}$  is a big challenge in this city. Furthermore, soil's desirable condition is due to low density of heavy metals.

Best quality in the individual health and treatment indicator was because of high percentage of children vaccination with a score of 100%, percentage of specialists, practitioners and assistances of doctors with a score of 100%, the necessary number of specialist and general hospital and clinic with a score of 88.8% and also low amount of pulmonary tuberculosis and malaria diseases with a score of 75%.

In the safety and security indicator, the city's middle ranking quality was due to the high states of car accidents with a score of 0 % and high quality of the minimum time for helping fire stations to casualties with a score of 75%. Middle ranking quality of social environment indicator was because of high divorce rate and desirable quality for family size with 0% and 100% scores. Best quality of education indicator was because of illiteracy rate with 80% score and 100% score of radio and television coverage across the city. Desirable quality of employment indicator was because of unemployment rate, inflation rate, and gini coefficient with scores of 75%, 50%, and 75%, respectively. Desirable quality of public service centers distribution was because of distribution of vegetable and fruit district's bazaars throughout the city with a score of 75%. High quality of urban infrastructures was due to phone landlines with a score of 100% and wastewater piping networks with a score of 100% (because of Isfahan's urban ago system), desirable quality of information technology centers and

recycling house of waste with a score of 66% on the other hand. High quality of transportation indicator was because of using public transportation for intercity travelling with a score of 83%, the desirable quality of average of expectation for buses in stops and share of bicycles in intercity travelling with a score of 66% (because of traditionally using of bicycles in Isfahan city), and also desirable quality of public transportation per capita with a score of 75%. Middle ranking quality of housing indicator was because of the number of family's ratio to housing units with a score of 50% and average size of housing units with a score of 66.6% in this indicator. In the main indicator of art, culture, and recreation, the city's desirable quality was due to library usage per capita with a score of 25%, the number of museums per 100000 people with a score of 33%, and the importance ranks of historical heritages with a score of 100%.

### **Conclusion**

The most important result and the main difference of this study with previous ones is comparative analysis of urban indicators presented in different countries. At first, some of the newest studies and similar experiences for evaluating urban environmental quality have been extracted. In the next stage, aforesaid indicators have been studied. Thus, a collection of useful indicators has been collected and categorized. It caused to update the indicators method. Hence, validity and stability of this method has been verified because of its use in different cities and the measuring capability of necessary characteristic via these indicators.

**Keywords:** indicators, Isfahan, quality, urban environment.

## Environmental Risk Assessment of Gotvand-Olia Dam at Operational Phase Using the Integrated Method of Environmental Failure Mode and Effects Analysis (EFMEA) and Preliminary Hazard Analysis

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### Introduction

Gotvand-Olia as one of the largest constructional projects in Iran has been constructed on the Karoun River, between Masjed Soleiman and Gotvand Regulatory dam in Khuzestan Province. It is situated in 382.8 km away from the river estuary at a distance of 25 km north of Shoushtar city. This study was conducted to identify and assess the risk of Gotvand-Olia dam on the environment at the operational phase. As a part of the management of water resources, the dam is one of the most important structures playing a major role in the regulation of surface flows, especially in the areas that have poor spatial and temporal distribution of rainfalls. Due to developments in dam construction in the world and particularly in Iran, the need to assess the environmental impacts of dams is very important. Environmental risk assessment is able to establish a relationship between the impacts of unwanted events with those that are not catastrophic. The quantitative risk assessment provides evident objectivity and transparency in the assessment of the impacts.

### Material and methods

The current study aims at assessing the risk of Gotvand-Olia dam at the operational phase. Accordingly, after reviewing the relevant literatures, field studies, and interviewing with expertise and research team, a questionnaire was designed to identify the potential risks during the operational phase. According to the studies conducted in the field of dam risks in the world and particularly in Iran as well as the technical and environmental reports on the Gotvand-Olia dam, the risk factors of the operational period were identified at first using the checklist of the PHA Method and were then assessed by EFMEA.

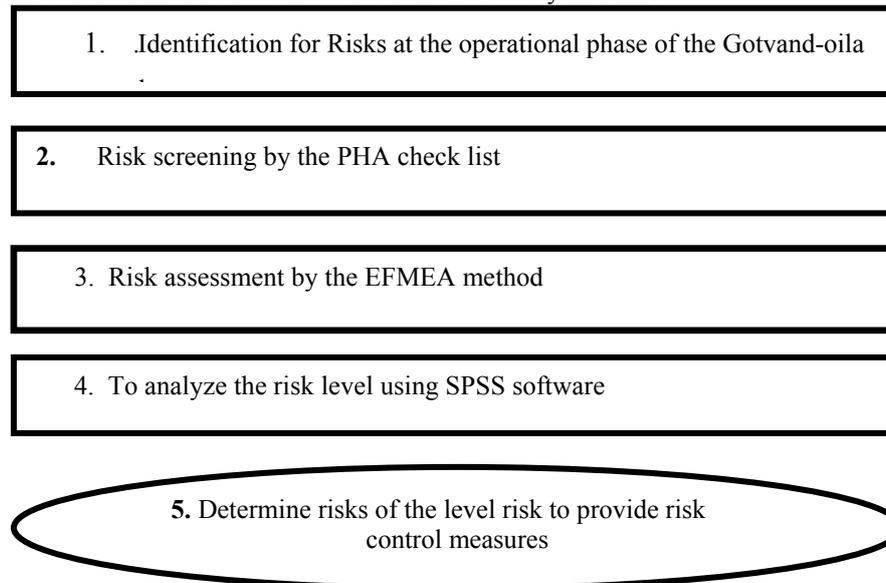


Figure 1. Study implementation of the risk assessment of the Gotvand-oila

In FMEA, techniques to obtain have degrees of severity, probability, and extent of contamination. After obtaining, the three number can be calculated through the formula Risk Priority Number (RPN)= Severity of risk  $\times$  Event Risk  $\times$  Extent of contamination. Subsequently, a list of potential risk factors at the operational phase was included in the questionnaire and placed at disposal of the individuals who were expert on dam and environment. Afterwards, considering the current situation of the study area, overall risk options at the operational phase (21 cases) were classified in the form of physicochemical, biological, socioeconomic, cultural, health-safety, and natural hazards using the PHA checklist. To make a decision on acceptance or rejection of risks, statistical methods were applied to prioritize risk factors and specify their hazardous level due to lack of prioritization of the risks in EFMEA. Accordingly, the high-level risks were identified.

The study implementation of the risk assessment of the Gotvand-oila was shown in the figure 1.

### Results and discussion

According to the identified risks, it can be concluded that reservoir inundation, extraction of borrow materials, transportation of vehicles and machineries, recreation and tourism as well as construction of infrastructure facilities are hazardous activities at the operational phase.

The risks at the operational phase of the Gotvand-oila by the FMEA method were shown in Table 1.

**Table 1. Risks at the operational phase of the Gotvand-oila by the FMEA method**

Level Risk	RISK Prior Number	Risk	series
H	320	Water salinization due to salt dome	1
H	288	Erosion & sedimentation in downstream of the dam	2
H	256	Generation of waste water and effluent by tourism & recreation	3
H	256	Generation of solid waste by tourism & recreation	4
H	256	Generation of waste water and in infrastructures	5
H	256	Generation of solid waste and industrial waste in infrastructures	6

The obtained results suggest that the highest RPN equal to 320 belongs to water salinization occurred due to the existence of salt domes. While borrowing materials, the highest RPN (tantamount to 288) is belonged to erosion and sediment. The risk level is high. In transportation using vehicles and machineries, the highest RPN (equal to 216) is allocated to the vehicle exhaust emissions. The risk level is moderate. Among tourism and recreational activities, the highest RPNs were assigned to the generation of wastewater and effluent as well as solid waste, both with the same RPN of 256. The risk level is high. Amongst activities related to the construction of infrastructures, the highest RPN (256) belongs to the generation of industrial wastewater and effluent. The risk level is high. A total number of 19 environmental risks were assessed and weighted by the EFMEA. Afterwards, they were analyzed by SPSS Software. Accordingly, upper and lower risk limits were determined 237.8 and 116, respectively. Majority of the risks identified at the operational phase of the Gotvand-Olia dam can be classified in medium-level category which devoted itself to 58% of the whole. In this respect, the low (L) and high (H) level risk categories comprising 10% and 32% of total risks, respectively, have the lowest share.

### Conclusion

The highest RPN (320) belongs to water salinization occurred due to the dam inundation while the lowest RPN (90) is related to providing an appropriate environment for growth and reproduction of insects (*Anopheles*) as well as soil compacting as a result of the agricultural development and the transportation of heavy machineries. The activity of Gachsaran formation leads to the depletion of soil impregnated with salt to the river that its impacts can be characterized in terms of salinity, total dissolved solids (TDS), total suspended solids (TSS), and electrical conductivity (EC). Given the importance of such a formation at the reservoir margins, the changes in the quality of river water at the operational phase can be justified. In this study, it is quite necessary to pay enough attention to the discharge of the Karoun River as well as regional droughts. It is also necessary to

consider a suitable place to dump soils containing salts extracted from upstream of the dam. In a second evaluation after the implementation of control and corrective measures, the highest risk of erosion and sedimentation downstream of the dam removal borrow materials (RPN= 168, a moderate risk level (M)) and the lowest risk is related to the oil spill equipment and the use of vehicles and machinery transporting operations (RPN=36, with a low risk level (L)).

Implementation of control and corrective measures of risks at the operational phase of Gotvand-oila was shown in Tabel 2.

**Table 2. Implementation of control and corrective measures of risks at the operational phase of the Gotvand-oila**

Corrective measures	Risk
Estimation assessment ecologic risk by attention to the environment impacts of Gachsaran formation.	Water salinization due to salt dome
Daily performance testing of water river quality.	
Daily sampling and monitoring of water river quality.	Erosion & sedimentation in downstream of the dam by removal borrow materials
Simulation erosion and salinization in the reservoir dam zone and precaution long time impacts.	
Program codification for clearing and correction borrow materials excavated in the Imam ZadeZaid zone.	
Program codification for green space development in the site.	

**Keywords:** EFMEA, Gotvand-Olia dam, environmental risk assessment, Khuzestan province, operational phase, PHA, reservoir dam, risk, risk prioritization.

## Game Theoretic Insights for Sustainable Common Poll Water Resources Governance (Case Study: Lake Urmia Water Conflict)

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### Introduction

Common pool water resources (CPWRs) face overuse and congestion due to increased competition for the non-excludability and subtractability nature of their use. In the CPWRs conflicts, beneficiaries base their actions on individual rationality which negatively affect all users eventually due to the lack of trust between them, their self-optimizing tendencies, and inadequate information about the consequences of their actions. Game theory provides a formal mathematical framework to strategic analysis of such conflict and to able presenting some institutions to prevent tragedy of commons. Lake Urmia is the most valuable ecosystem located in the same name basin in Iran. In the recent years, the basin's upstream water resources faced to overuse due to an increase in the attitudes of parties to gain more economic benefits from agriculture activities which led to conflicts as well as threats to Lake Urmia's life. The literatures which studied this environmental crisis are limited with respect to understanding strategic interactions between the actors and how such interactions may affect the results of the Lake Urmia water conflict.

### Materials and methods

In order to study the Lake Urmia water conflict, basic information were prepared through a review of the relative literatures, the technical documents, and the news reports. These collected data were completed by referring to experts opinions and finally the conflict was modeled and analyzed based on the GMCR process of resolving conflicts. As a non-cooperative game theoretical model, the Graph model for conflict resolution (GMCR) was developed through a combination of extensive form of conflict analysis and graph theory. Figure 1 outlines the GMCR process of resolving conflicts which involves two main stages including modeling and analyzing. The modeling stage includes defining decision makers and their options, removing infeasible states of the conflict, specifying allowable transitions from each state for each player, and finally defining the relative preferences of each player over each state. In the analyzing stage, stability of the feasible states for each player is first analyzed using the formal mathematical definitions named non-cooperative solution concepts. The second stage is followed by finding the equilibria or likely outcomes of the conflict (states which are stable for all stakeholders under a given solution concept). If a given state is known as equilibrium under a range of solution concepts, then it is a strong equilibrium with a higher likelihood of being the final outcome of the game. After that, some alternative scenarios are defined in order to examine the sensitivity of the results to changing input information. Finally, strategic insights from decision makers' interactions are presented to help them for better decision making.

### Discussion of results and conclusions

As can be seen in Table 1, there were five decision makers with seven options in the Lake Urmia water conflict. The number of total states of the conflict was 128 which reduced to 72 after infeasible states were removed. Then, allowable moves from a given state to each other and the player's preferences were defined respectively. Based on the DM's preferences, the Ministry of Agri-Jihad (MAJ) has preferred to continue its new agriculture development projects while it has tended to protect the basin's farmers to improve their cultivation and irrigation styles. Although the Ministry of Energy (MOE) has interested to implement interbasin water transformation projects but it has not liked to stop its new water resources development plans. The Basin's Provinces (BP) have disagreed to stop their new local water and agricultural development plans. Farmers of the basin (F) have liked to continue their illegal overuse from upstream water resources of the basin and the Central Government (CG) has preferred to take no action to force MAJ, MOE, and BP to stop their new development plans. After the conflict

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was modeled, the stability analysis was applied through non-cooperative solution concepts followed by an alternative preference scenario developed in order to find how changes in decision makers' preferences affect the initial results. According to Table 2, eight outcomes became known as the game equilibria. The results indicated that the state 6, which is current situation of the real world conflict as well as selected as status quo of the analysis, was suggested as the most likely outcome of the game in the initial analysis by GMCR. It means that Lake Urmia crisis mainly rooted in individual rationality based behaviors of beneficiaries which appeared as they persisted on increasing their shares from common poll resources of the basin upstream. Also, it proposed GMCR as an effective and applicable tool for strategic analysis and sustainable common poll water resources governance. Based on the results of sensitivity analysis to move out the status quo, the Central Government should change his initial preferences through strong interference in the conflict and force the parties to stop their upstream new developments. If such situation occurs, the state 68 will be chosen as the final resolution of this conflict.

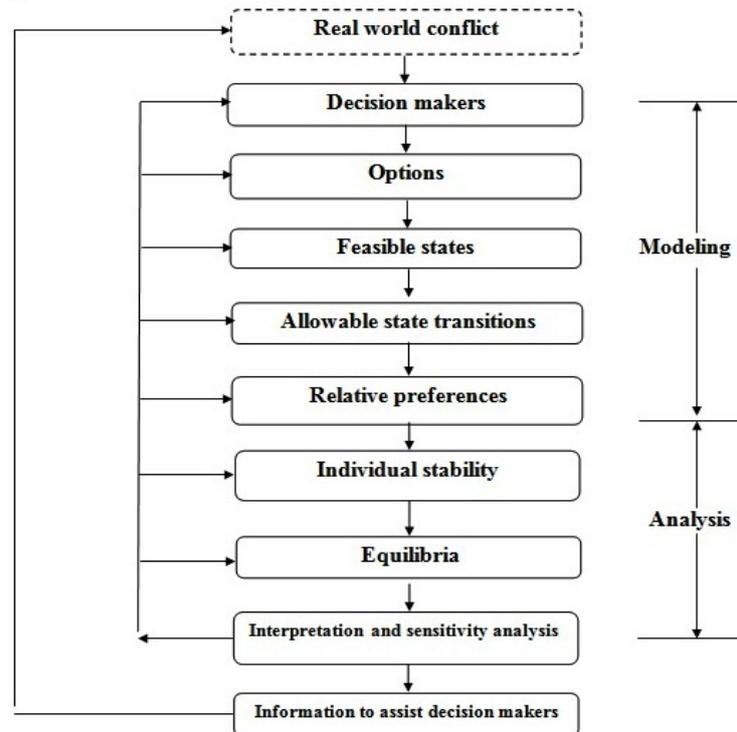


Figure 1. The GMCR process of conflict resolution (Fang et al., 1993)

Table 1. DM's, options and status quo in Lake Urmia water conflict

DM's	Options		Status Quo*
MAJ	1	Protect the farmer of the basin to improve their cultivation and irrigation styles	Y
	2	Stop new agricultural activities and watershed management development plans	N
MOE	3	Release more water from dam reservoirs into the lake, executing interbasin water transfer projects	Y
	4	Stop new water resources development plans	N
F	5	Stop illegal overuse from basin's upstream water resources	N
BP	6	Stop their new local development plans (accept allowed water rights)	N
CG	7	Order MAJ, MOE and BP to stop their new upstream development plans	N

\* Note: Y= YES: option is taken by player; N= NO: option is not taken by player

Table 2. Most likely outcomes of Lake Urmia water conflict

DM's	Options	Equilibria							
		Initial analysis				Sensitivity analysis			
		1	2	5	6	68	67	66	65
MAJ	1	N	Y	N	Y	Y	N	Y	N
	2	N	N	N	N	Y	Y	Y	Y
MOE	3	Y	Y	Y	Y	Y	Y	N	N
	4	N	N	N	N	Y	Y	Y	Y
F	5	N	N	N	N	N	N	N	N
BP	6	N	N	N	N	Y	Y	Y	Y
CG	7	N	N	N	N	Y	Y	Y	Y

**Keywords:** common poll water resources, Lake Urmia, Game theory, graph model for conflict resolution, sustainable governance.

## Hydrogeochemical Analysis of Bidkhan Stream of Bardsir (Southeast Iran) Using Principal Component and Cluster Analyses

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### Introduction

Thermodynamically, the surface waters in mountain environments are unstable and their chemical composition is a reflection of water-rock interactions. Few studies have also been undertaken on the geochemistry of the surface waters in mountain environments. Hence, this paper deals with the source of elements as well as the chemistry of the stream which drains from the caldera of Bidkhan volcano.

The Bidkhan is an inactive stratovolcano having a caldera located at southeast Iran at a distance of 115 Km from Kerman (40 Km southeast of Bardsir town). Its geographical coordinates include 56°, 25' to 56°, 30' eastern longitude and 29°, 35' to 29°, 40' northern latitude. This volcano lies at the southeastern part of the volcanic belt of central Iran (Orumieh-Dokhtar belt). The Bidkhan volcano occupies an area of 400 km<sup>2</sup> and its highest summit lies at about 3800 m above mean sea level. The Bidkhan stream drains its caldera. The caldera lies in almost 12 kilometers of the course of the Bidkhan stream and supplies several villages in its course. There is no hydrometric station along this stream, but based on field observations, the highest flow is about 600 L/s in April. This stream usually dries out in the August-December period. Its average flow is about 610 L/s. According to the undertaken measurements, the water temperature varies from 15 to 20 C° along its course in summer times. The pH values range from 6.9 to 7.4.

### Geology

Surge deposits which cover unconformably Eocene rocks are considered as the first products of the eruption of this volcano. According to geochronological studies undertaken by Khalili et al (2008), its activity has initiated about 13 million years ago. This volcanic structure consists of alternatives of andesitic-dacitic and rhyolitic lavas as well as pyroclastic and epiclastic deposits as the products of several cycles of its activity. After ceasing volcanic activity, a period of plug and dyke intrusion has taken place. This volcano has entered an erosion phase since about 10 million years ago.

### Materials and methods

In this study, 12 water samples were collected from the Bidkhan stream as shown in Fig 1. Polyethylene bottles were used at each sampling point, and three separate samples, for major anions, major cation, and metals, were taken. In order to prohibit ion precipitation and biotic activities, the cation and metal ones were acidified using nitric acid. The temperature and pH were measured in the field and geographical locations were determined by a GPS device. Major ions were measured in the laboratory of Regional Water Organization of Kerman and heavy metals were measured in the central laboratory of Shahid Bahonar University. Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup> were analysed by titration method and sodium by flame photometry.

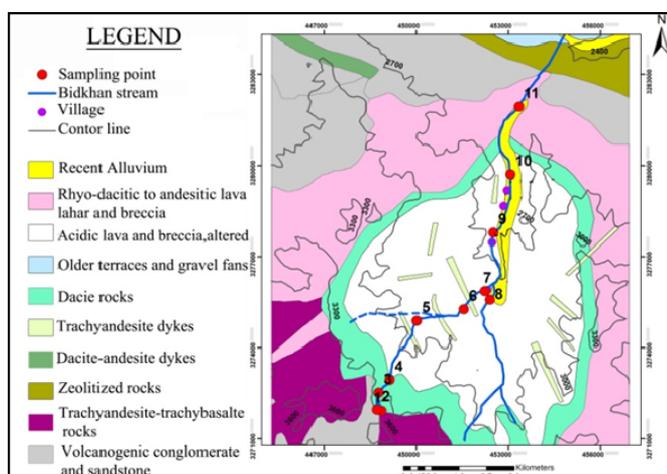


Figure 1. Location of sampling points in Bidkhan river on the geological map of the area

Sulfate concentration was determined using gravimetric assay. Finally, the metals were analysed using ICP-OES technique. In order to determine the source of analytes, statistical methods of PCA and CA as well as correlation matrix were employed.

### Results and discussion

In PCA test, four factors were identified. Factor 1 includes  $\text{Li}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  cations and  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  anions. Fe, Mn and Al comprise factor 2. Factor 3 includes V and pH. And, lastly, Cd is located lonely in factor 4 (Table 1).

Fig. 2 shows the cluster analysis of the components. In the cluster analysis,  $\text{Li}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Ba}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  form a major cluster. The other important cluster includes Fe, Mn and Al. Vanadium and pH make up another cluster and Cd is almost isolated from the other components (Fig. 2).

Overall, comparison of the results of PCA and CA tests supports each other and both are matched with correlation coefficients. The elements and compounds in the factor 1 indicate the influence of the major processes such as rain water chemistry, silicate hydrolysis, and possibly pyrite oxidation. Those located in the factor 2 (Fe, Mn and Al) represent release from silicate hydrolysis and pyrite decomposition (Fe), but all these elements are very insoluble and precipitate as oxides and hydroxides.

Those comprising the factor 3 (vanadium and pH) exhibit a strong dependence on V with pH changes. Cd lonely lies in the factor 4 highlighting major differences in its chemical behavior in comparison with the other analytes.

Detection limit for Zn, Cu, and Ni elements is 10  $\mu\text{g/l}$ . Also, detection limits for Mo and Cr are 2 and 1  $\mu\text{g/l}$ , respectively. Concentration of these elements in all samples is not only below the detection limits but also lower than the EPA and WHO standards. The detection limits for Arsenic and Pb are 5 and 10  $\mu\text{g/l}$ , respectively. There is only one sample higher than the detection limits in both of these elements. Arsenic concentration just in this sample reaches to 8.64  $\mu\text{g/l}$  that is lower than the EPA and WHO standards. The Pb concentration in this sample is 14.19  $\mu\text{g/l}$  that is lower than the EPA standard and higher than the WHO standard. The concentration of V, Ba, Li, Sr, and Cd elements was described in the following.

The vanadium concentration ranges from less than 20 to 59.22  $\mu\text{g/l}$  with a median of 24.03  $\mu\text{g/l}$ , which is 4.48 times higher than its average content in the rivers across the world. According to the studies undertaken by Khalili (2012) and Atapour (2008), the average concentration of this element in the rocks of this area is about 3.75 times higher than the average content in the intermediate rocks. High-V rocks in the studied area have led to the enrichment of waters with respect to this element. There are not any standards for the V concentration in waters. So, we compared the concentration of this element with drinking water in other countries. The result is that the concentration of this element in the Bidkhan stream is higher than that of drinking water in other countries.

The barium and lithium concentrations range from 0.28 to 23.56 with a median of 13.01  $\mu\text{g/l}$  and 1.08 to 20.85 with a median of 5.86  $\mu\text{g/l}$ , respectively. These medians are, respectively, 13.01 and 1.7 times higher than the average content in the rivers across the world. The highest concentration of these elements is lower than the EPA and WHO standards.

Strontium concentration ranges from 25.47 to 394.14  $\mu\text{g/l}$  with a median of 145.767  $\mu\text{g/l}$ , which is 2.9 times higher than the average content in the rivers across the world. According to the studies undertaken by Khalili (2012) and Atapour (2008), the average concentration of this element in the rocks of the studied area is about 2.2 times higher than the average content in the intermediate rocks. Hence, the strontium concentration in the Bidkhan river reflects the concentration of this element in the rocks. There is not any standard for the Sr as well. Hence, we compared the concentration of this element in the Bidkhan stream with the one in drinking water in other countries which indicates similar situations.

The cadmium concentration ranges from less than 0.5 to 4.54  $\mu\text{g/l}$  with a median of 0.38  $\mu\text{g/l}$ . Samples 2 and 9 are slightly higher than the maximum level of cadmium in natural waters (3  $\mu\text{g/l}$ ). The highest Cd concentration is lower than the EPA standard and higher than the WHO standard.

Table 1. PCA of elements in the Bidkhan river

Parameter	Rotated Component Matrix <sup>a</sup>			
	Component			
	1	2	3	4
Ba	0.59			
Li	0.96			
Sr	0.96			
Ca <sup>2+</sup>	0.65			
Mg <sup>2+</sup>	0.78			
Na <sup>+</sup>	0.93			
HCO <sub>3</sub> <sup>-</sup>	0.81			
SO <sub>4</sub> <sup>2-</sup>	0.83			
Cl <sup>-</sup>	0.77			
Al		- 0.89		
Fe		- 0.92		
Mn		- 0.93		
V			0.86	
PH			0.83	
Cd				0.82

Extraction Method: Principal Component Analysis.  
Rotation Method: Varimax with Kaiser Normalization.  
a. Rotation converged in 6 iterations.

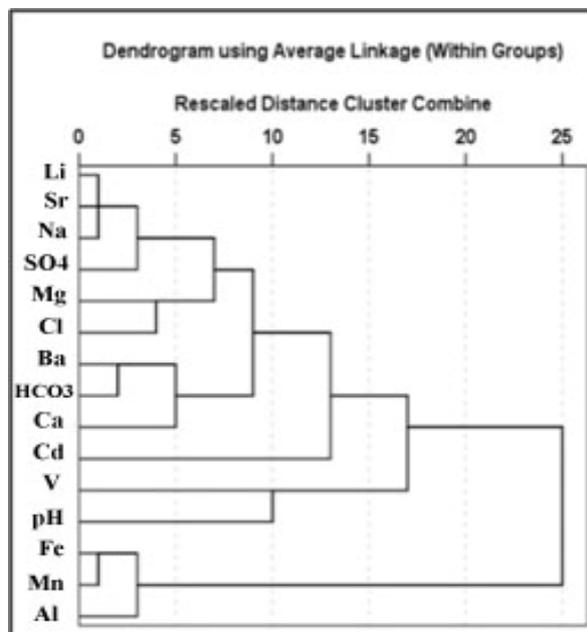


Figure 2. Cluster analysis of elements in the Bidkhan river

### Conclusion

In all, although the source of some elements is rain water, the main source of major cations as well as heavy metals is the hydrolysis of silicates. Since igneous rocks are poor in chlorine, the main source of this element is the rain water. The sulfate cation may originate from the Pyrite oxidation and/or rain water.

Separation of the analytes in four factors revealed that they follow the basic rules governing their concentration in waters. Also, the concentration of some elements such as Ba, Li, Sr, and V is higher than their average concentrations in river waters. As an example, V is 5 times higher in concentration than the average. Some elements such as Cu and Cr have not been solved due to Eh and pH conditions. The presence of Al, Mn, and Fe hydroxides in bottom sediments leads to adsorption of some elements. So, it is proposed that the concentration of elements be determined in bottom sediments to get a better idea on some processes such as adsorption and desorption.

**Keywords:** Bidkhan stream, cluster analysis, hydrogeochemistry, principal component analysis, volcanic rocks.

## Uptake and Removal Capability of Toxic Heavy Metals From the Industrial Discharge of Mobarakeh Steel Complex by Metal Accumulating Plants

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### Introduction

Heavy metals are largely found in dispersed form in rock formations. Industrialization and urbanization have increased the anthropogenic contribution of heavy metals in the biosphere. Heavy metal pollution not only affects the production and the quality of crops, but also influences the quality of the atmosphere and water bodies, and threatens the health and life of human beings. Clean-up technologies have been developed for the removal of heavy metals but often these are expensive or have some environmentally deleterious consequences. Phytoremediation emerged in the early 1980s is an important technology for remediation of contaminated sites. One of the most promising phytoremediation technologies is phytoextraction using hyperaccumulators to remove heavy metals from contaminated soils. However, the known hyperaccumulator plants usually accumulate only a specific element and are usually small. Recently, most attention is focused to the plants that produce high biomass and are tolerant to the soils polluted with heavy metals.

*T. caerulescens* was found to colonize areas with high Cd, Cu, Pb, and Zn present in soils due to mining. *M. chenopodiifolia* has good potential for absorbing Pb and Zn. *Eruca sativa* is tolerant to soil pollution with heavy metals and can accumulate Pb and Cd from contaminated soils. *B. napus* accumulated cadmium and zinc and translocated these elements into the harvestable parts of the plant. *S. nigrum* is often found in contaminated areas. It has previously been identified as a Cd hyperaccumulator. *H. annuus* is known for its high biomass yield. In addition, it is tolerant to soil pollution with heavy metals. *Z. mays* produce high biomass as well.

In this study, we studied the capability of stability, growth, and uptake of heavy metals by means of *T. caerulescens*, *Z. mays*, *H. annuus*, *E. sativa*, *B. napus*, *S. nigrum*, and *M. chenopodiifolia* on the industrial discharge of Mobarakeh Steel Complex.

### Materials and methods

Mobarakeh Steel Company is located 75 km south west of Isfahan, near the city of Mobarakeh, Isfahan Province, Iran. It is Iran's largest steel maker and one of the largest industrial complexes operating in Iran. Three type effluents (first and second type and galvanized unit) were taken from separated lagoons.

The pH of the soil was determined using a glass electrode after 10 g of soil had been stirred well in 30 ml distilled water in a beaker and allowed to stand for about 30 min. In the first experiment, pots (9 cm diameter) fill up with the first and second types and the galvanized unit effluents separately. The seeds of each plant (*T. caerulescens*, *Z. mays*, *H. annuus*, *E. sativa*, *B. napus*, *S. nigrum* and *M. chenopodiifolia*) were then sown on the pots. The pots were irrigated with distilled water every three days for six weeks. The seedlings were irrigated with 100 ml nutrient solution containing 2.46 g/l KH<sub>2</sub>PO<sub>4</sub>, 4.72 g/l KNO<sub>3</sub>, and 0.27 g/l Ca(NO<sub>3</sub>)<sub>2</sub> every eight days instead of the distilled water. For the analysis of plant dry matter, the leaf materials were washed well with double-distilled water and dried at 70°C for 48 h. About 0.1 g of dry leaf sample was added to a 25 ml beaker and ashed in a muffle furnace for 6 h at 500°C. The ash was taken up in 10 ml 10% HNO<sub>3</sub> and the digest was finally made up to 50 ml in 10% HNO<sub>3</sub>. The solutions were analyzed for elemental composition by AAS. All soil samples were air-dried and sieved to <2 mm. For the analysis of total elements, sub-samples of 4-5 g were ground to pass through a 80 mesh sieve and then oven-dried at 70°C. A further sub sample of 0.5 g was transferred to a Kjeldahl digestion tube for extraction with 10 ml of a 3:1 HCl/HNO<sub>3</sub> mixture. Tubes were left at room temperature overnight and were then placed in a heating block. Each tube was covered with an air condenser and refluxed gently at 100°C for 1 h. After cooling, the digests were filtered through a moistened filter

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paper into a 50 ml volumetric flask. The flasks were made to volume with distilled water. Ten milliliters of the digest were added to 15 ml tubes and the analysis for Zn, Pb, Cr, Cd, and Ni was performed by atomic absorption spectrophotometry (AAS, Shimadzu model AA 6200).

## Results

The results indicated that in the first type of effluent the amounts of heavy metals were relatively high as follow; Zn ( $72 \text{ mg kg}^{-1}$ ), Pb ( $20 \text{ mg kg}^{-1}$ ), Cr ( $28 \text{ mg kg}^{-1}$ ), Cd ( $20 \text{ mg kg}^{-1}$ ), and Ni ( $118 \text{ mg kg}^{-1}$ ). In the second type of effluent, these amounts were  $68 \text{ mg Zn kg}^{-1}$ ,  $7 \text{ mg Pb kg}^{-1}$ ,  $19 \text{ mg Cr kg}^{-1}$ ,  $21 \text{ mg Cd kg}^{-1}$ , and  $115 \text{ mg Ni kg}^{-1}$ . In galvanized unit effluent, these amounts were high; Zn ( $353 \text{ mg kg}^{-1}$ ), Pb ( $55 \text{ mg kg}^{-1}$ ), Cr ( $1768 \text{ mg kg}^{-1}$ ), Cd ( $22 \text{ mg kg}^{-1}$ ) and Ni ( $114 \text{ mg kg}^{-1}$ ). The pH of the first and second types and the galvanized unit effluent were 8.4, 8.8, and 9.2, respectively (Table 1).

**Table 1. The amounts of heavy metals ( $\text{mg kg}^{-1}$ ) and pH in three types of effluent**

Type of effluent	Zn	Pb	Cr	Cr	Ni	pH
first type	$72 \pm 0.3$	$20 \pm 10.1$	$28 \pm 9.6$	$28 \pm 9.6$	$118 \pm 5.1$	8.4
second type	$68 \pm 3.8$	$7 \pm 2.5$	$21 \pm 0.8$	$19 \pm 19.3$	$115 \pm 1.8$	8.8
galvanized unit	$353 \pm 109.5$	$55 \pm 8.7$	$22 \pm 0.6$	$512.4 \pm 1767$	$114 \pm 8.4$	9.2

Among species planted on the first type of effluent, *H. annuus* had more dry weight ( $910 \text{ mg/plant}$ ) and *M. Chenopodiifolia* and *T. caerulescens* had less dry weight ( $1 \text{ mg/plant}$ ). Among the species planted on the second type of effluent, *H. annuus* had more dry weight ( $600 \text{ mg/plant}$ ) and *M. Chenopodiifolia* and *E. sativa* had less dry weight ( $51 \text{ mg/plant}$ ). Among the species planted on the effluent of the galvanized unit only *Z. mays* was able to grow. Dry weight of these species was  $900 \text{ mg/plant}$  as shown in Table 2.

**Table 2. Dry weight of the species planted on three type effluents in mg per plant**

Type of effluent	<i>Z. mays</i>	<i>H. annuus</i>	<i>T. caerulescens</i>	<i>S. nigrum</i>	<i>E. sativa</i>	<i>B. napus</i>	<i>M. Chenopodiifolia</i>
first type	$800 \pm 12$	$910 \pm 13.2$	$1 \pm 0.2$	$10 \pm 3$	$30 \pm 5$	$30 \pm 2.1$	$1 \pm 0.1$
second type	$170 \pm 10$	$600 \pm 12$	Not grow	Not grown	$51 \pm 7.7$	Not grown	Not grown
galvanized unit	$900 \pm 13$	Not grown	Not grown	Not grown	Not grown	Not grown	Not grown

The highest accumulation of Zn was taken up by *T. caerulescens* ( $91.5 \text{ mg/kg}$ ). The most accumulation of Pb by *T. caerulescens* was  $74 \text{ mg/kg}$ . The most accumulation of Cr by *T. caerulescens* was  $637 \text{ mg/kg}$ . The most accumulation of Cd by *B. napus* was  $6.6 \text{ mg/kg}$ . The most accumulation of Ni by *T. caerulescens* was  $226.3 \text{ mg/kg}$ .

In the second type of effluent, the most accumulation of Zn and Pb by *Z. mays* was  $40.1 \text{ mg/kg}$  and  $117.2 \text{ mg/kg}$ , respectively. The most accumulation of Cr by *E. sativa* was  $117.2 \text{ mg/kg}$ . Amount of Cd uptaken by *Z. mays*, *H. annuus*, and *E. sativa* were  $12.2 \text{ mg/kg}$ ,  $14.9 \text{ mg/kg}$  and  $14 \text{ mg/kg}$ , respectively. The most Ni accumulation by *E. sativa* was  $121.2 \text{ mg/kg}$ .

*Z. mays* was the only species that could grow on the galvanized unit effluent. It could accumulate Zn, Pb, Cr, Cd, and Ni to  $57 \text{ mg/kg}$ ,  $68 \text{ mg/kg}$ ,  $309 \text{ mg/kg}$ ,  $32.5 \text{ mg/kg}$ , and  $55.4 \text{ mg/kg}$ , respectively.

## Discussion

In some countries excessive concentrations of toxic heavy metals such as Zn, Pb, Cd, Cr, and Ni in soils in mining areas and around smelters are the sources of serious environmental and health hazards. Among seven

species planted on the first type of effluent, *T. caerulescens* could accumulate Zn, Pb, Cr, and Ni to a large extent and it could almost grow on the industrial discharges. The hyperaccumulator plant *T. caerulescens* is able to grow on the contaminated soils by heavy metals. These species have received much attention as a potential candidate for phytoextraction of Zn and Cd from the contaminated soils. *B. napus* could accumulate Cd to a large extent. Brassica family (*B. napus*, *Brassica juncea* and *R. sativus*) has been suggested for phytoremediation of the heavy metals. Four species (*Z. mays*, *H. annuus*, *E. sativa* and *B. napus*) were able to grow well and uptake heavy metals from all types of effluents. Among seven species planted on the second type of effluent, *Z. mays* could accumulate Zn and Pb and *E. sativa* could accumulate Cr and Ni to a large extent. *H. annuus* was the only species tolerant on the effluent and could produce high biomass yield. Hence, these species have been described or proposed for phytoremediation of the heavy metals. Among seven species planted on the effluent of the galvanized unit, *Z. mays* was the only one able to well grow and accumulate Cr to a large extent.

### Conclusion

The acquired results indicated that *Z. mays*, *H. annuus*, *E. sativa*, and *B. napus* were able to well grow and uptake heavy metals from the first type effluent. Among seven species planted on the second type of effluent, *H. annuus* was the best species for phytoremediation. For phytoremediation of heavy metals from the galvanized unit effluent, *Z. mays* was the only suitable species.

**Keywords:** industrial effluent of Mobarakeh Steel Complex, heavy metals, phytoremediation.

## Optimization of Malachite Green Biosorption by Green Microalgae from Aqueous Solutions

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### Introduction

Malachite green (MG) has been used as a food coloring agent, food additive, medical disinfectant as well as a dye in silk, wool, jute, leather, cotton, paper, and acrylic industries. It is also extensively used as a topical fungicide and ectoparasiticide in aquaculture industries throughout the world. The findings reveal that this dye has now become one of the most controversial compounds used in aquaculture due to the risks it poses on the consumers, including its effects on the immune and reproductive systems as well as its genotoxic and carcinogenic potentials. Despite being banned in several countries, the dye is still being used in many parts of the world due to lack of a proper alternative. Thus, we must also focus our attention on ways for reducing malachite green from aquaculture and industrial wastewaters. Different methods are available for the remediation of dye wastewaters. These include physicochemical methods such as chemical oxidation, precipitation, coagulation, filtration, electrolysis, and photodegradation. The major disadvantage of the physicochemical methods are high operational cost, limited versatility, interference by other wastewater constituents, and less adaptability to a wide range of dye wastewaters. Sorption on activated carbon is an effective method for the removal of color, but it is an expensive method. The development of efficient and environmentally friendly technologies to decrease dye content in industrial wastewater to acceptable levels at an affordable cost is of great importance. In recent years, a number of studies have been focused on some bacteria, fungi, yeasts, and micro/macroalga. Biosorption of MG in the presence of algae such as *Caulerpa racemosa* cylindracea, *Cosmarium* sp., *Pithophora* sp., *Hydrilla verticillata*, and *Chara* sp. has been reported previously. The aim of this study was to investigate the biosorption characteristics of green microalgae *Scenedesmus quadricauda* and *Chlorella vulgaris* for the removal of MG dye. The effects of such process parameters as initial MG dye concentration (mg/L), initial solution pH, algae amount (mg/L), and contact time (min) on the dye biosorption were analyzed using Box–Behnken design in this work.

### Materials and methods

MG stock solution was prepared by dissolving 100 mg MG (Serva, United States) in 1 L deionized water. All the other MG solutions were prepared by diluting the MG stock to obtain different concentrations ranged from 0.1 to 10 mg/L. The pH was adjusted using diluted NaOH and HCl solutions. The algal species were acquired from natural fresh water, Zayandeh-Rood River, Isfahan province, Iran, in November 2010. Algae were grown in several 2 L conical flasks containing Bold's basal medium (BBM) in order to obtain algal stock. The cells were cultured at 25±2°C temperature, 12h L: 12h D photoperiod and a light intensity of 80 µmol photons/m<sup>2</sup>/s for a maximum 10 day exposure period. The algal biomass was centrifuged and the remaining biomass dried at 50°C for 48 h. The dried cells, which were ground, produced a uniform material which was stored in the desiccator for further use. Batch sorption experiments were carried out at 26 ± 2°C on a rotary shaker (Dragon LAB, sk-330-pro, Germany) at 135 rpm using 100 ml conical flasks. Malachite green sorption studies were conducted by taking different amounts 2, 4 and 6 mg of algal biomass in 50 ml conical flasks containing 2, 6 and 10 mg/L of MG at different initial solutions, pH 3, 4.5, and 6, and at different contact times of 10, 50, and 90 min. After the end of predetermined time, the resulted solutions were filtered through a 0.2 µm membrane filter (Orange

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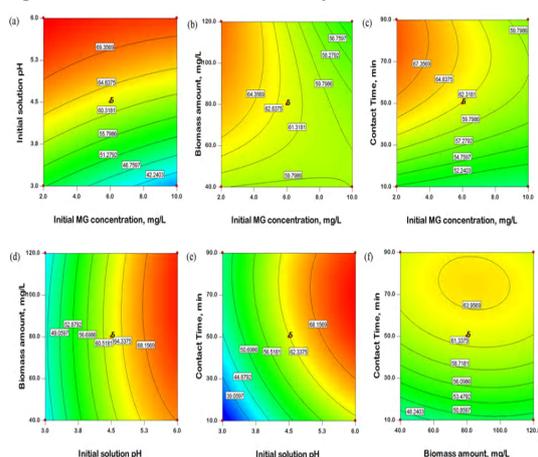
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Scientific, GyroDisc CA-PC, Belgium) and analyzed quantitatively. The remaining MG was determined with a spectrophotometer (Jenway, 6400 spectrophotometer, England) at the maximum sorption wavelength, ( $\lambda_{\max} = 618 \text{ nm}$ ). Box-Behnken Design, which is well suited for fitting a quadratic surface and usually works well for the process optimization, was used for the experimental design. Total 29 experiments were designed by Design Expert software (Version 8.0.4, Stat-Ease, Inc., Minneapolis, United States) statistical package.

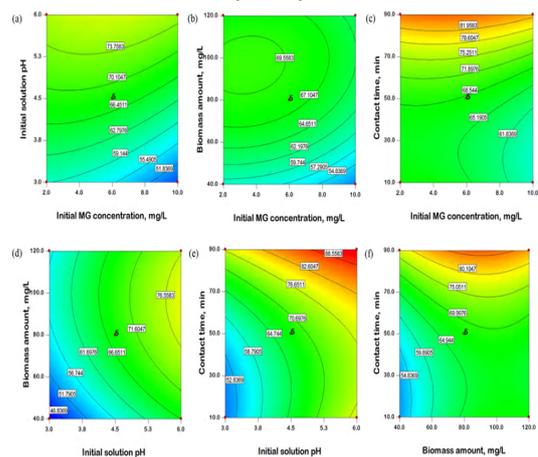
## Results and Discussion

The second-order polynomial analysis and quadratic model were employed to find out the relationship between variables and responses. The regression equation obtained after the ANOVA showed that the correlation coefficient ( $R^2$ ) was 0.9918 and 0.9936 for the MG removal percentage of *S. quadricauda* and *C. vulgaris*, respectively. However, in this case,  $R^2$  values of 0.9918 and 0.9936 implied a sample variation of 99.18% and 99.36% were attributed to the variable and only 0.82% and 0.64% of the total variance could not be explained by the model.

Therefore the high  $R^2$  value, significant  $F$ -value, and insignificant lack-of-fit  $P$ -value indicate high adequacy and validity of the models in predicting the MG removal by *S. quadricauda* and *C. vulgaris*. Therefore, these models were used for further analysis. The MG removal efficiency of algae decreased with an increase in initial MG concentration. The reason for the decrease in the MG removal efficiency can be attributed to the fact that all the algal biomass had a limited number of active sites, which would have become saturated above a certain initial MG dye concentration. In other words, as dye molecules are adsorbed on all active sites of algal biomass, the higher concentration of MG dye would have no impact on the removal efficiency of dye.



**Figure 1.** Contour plots for MG removal efficiency onto *S. quadricauda* biomass: a) pH versus MG conc.; b) biomass versus MG conc.; c) time versus MG conc.; d) biomass versus pH; e) time versus pH; and f) time versus biomass.



**Figure 2.** Contour plots for MG removal efficiency onto *C. vulgaris* biomass: a) pH versus MG conc.; b) biomass versus MG conc.; c) time versus MG conc.; d) biomass versus pH; e) time versus pH; and f) time versus biomass.

The removal efficiency of MG rapidly increases with an increase in initial pH of solution from 3.0 to 6.0. The pH of the solution plays an important role in the whole dye sorption process and particularly on the dye sorption efficiency. With increasing pH, the  $\text{OH}^-$  ion concentration in the system increases and the surface of algae achieves a negative charge by adsorbing  $\text{OH}^-$  ions. Negatively charged surface sites onto algal biomass favored the sorption of the cationic dye molecules such as MG due to electrostatic attraction. Furthermore, the initial pH of dye solution affected not only the surface charge of the biosorbent, but also may also have increased the degree of ionization of the dye present in the solution and the dissociation of functional groups on the active sites of the biosorbent. Thus, these effects facilitate electrostatic interaction between algal biomass and the positively charged cationic dyes leading to maximum MG removal.

Also, the removal of MG dye increased with increasing biomass amount of algae. After dye removal reached the optimum sorption points, the dye sorption decreased slowly. The reason for this observation is thought to be the fact that the increase in algal biomass up to optimum points gives more surface area and more binding sites for sorption of the MG ion on the surface of algae; thereafter, the biomass particle aggregation in higher biomass results in increase of diffusional path length and a decrease in total surface area of the biosorbent and the removal efficiency of dye.

These results revealed that biosorption of MG was strictly time dependent. In this condition, a large quantity of dye has been adsorbed onto biomass after a relatively short contact time, where the main sorption of molecules was noticed within the first 20 min of the experiments; thereafter, the sorption rate decreased gradually and the sorption reached equilibrium in about 90 min. The reason for this observation can be the fact that at the beginning, the dye molecules were adsorbed externally and the biosorption rate increased rapidly. When the external surface became saturated, the dye molecules adsorbed into the porous structure of the biomass and finally, at some point in time, reached a constant value where no more dye was adsorbed from the solution. At that time, the amount of dye being adsorbed onto the biomaterial was in a state of dynamic equilibrium with the amount of dye desorbed from the biosorbents.

**Keywords:** biosorption, *Chlorella vulgaris*, malachite green, response surface methodology, *Scenedesmus quadricauda*.

## Simultaneous Application of Fenton – Electrochemical Reactor for Removal of Organic Loading in Biological Waste Sludge

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### Introduction

Wastewater treatment using activated sludge process (ASP) produces huge amounts of sludge that must be treated by efficient methods. Wastewater sludge handling is one of the most important economic-technical challenges of wastewater treatment projects. Conventional methods for this purpose are very time consuming, expensive and in lots of cases have limited success. In recent years the electrochemical oxidation techniques have been progressively used for water and wastewater treatment process. Many reports showed that these methods are very effective to eliminate or decrease the organic loading content of wastewater and sludge. Combination of electrochemical reactions and Fenton process has widely been studied for the destruction of organics and bio-refractory pollutants contained in industrial wastewater by highly oxidative hydroxyl radicals formed from reaction of  $H_2O_2$  with  $Fe^{2+}$ . This method offers more advantages than the chemical Fenton process due to the high efficiency of Fenton reagents (e.g.,  $H_2O_2$ ) utilization and lower retention time. The integrated Fenton and electrochemical reactor were used to reduce concentration of volatile suspended solids in sludge. High consumption rate of divalent iron ions is one of the disadvantages of Fenton method compared with its reduction. In this research, the electrochemical method has been used to solve this problem. The electrochemical method increases the reduction rate of divalent iron by converting the trivalent iron ions into the bivalent ones and it reduces the production of iron sludge. In this research, the effective parameters including ratio of iron to hydrogen peroxide, pH, retention time, concentration of hydrogen peroxide and the amount of electric current were investigated.

### Materials and methods

In the present study we have evaluated the efficiency of Fenton-Electrochemical process in reduction of organic contents of Secondary Sludge of Mahallati ASP wastewater treatment plant. This plant is located in Tehran, with treatment capacity of  $4800m^3$  per day and operates in extended aeration process. Table 1 shows the specifications of the investigated sludge. Our reagents were  $H_2O_2$  and  $Fe^{2+}$ .

The evaluated Fenton-Electrochemical reactor has been shown in figure 1. The reactor contains two graphite anodes and two graphite cathodes. The electrodes dimensions were  $1mm \times 140mm \times 60mm$ , and the distance between them is 1.5 cm. The volume of reactor has been selected 0.9 L. We used the mechanical mixer instead of electromagnetic stirrer because of the sensitivity of  $Fe^{2+}$  ions to electromagnetic materials. The temperature during the test was between 13.8 and 15.6 °C. All tests were conducted according to standard methods (APHA, 1999) and each part of experiments was repeated three times.

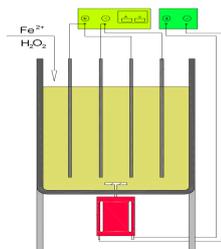


Figure 1. the evaluated EF reactor

Table 1. Investigated Sludge Specifications

property	Value
pH	6.53-7.33
Temperature(°C)	13.8-15.6
COD (mg/lit)	6051-11164
VSS ( mg/lit)	3536-7782
VS ( mg/lit)	4086-8382
TSS (mg/lit)	4088-8432
VSS/TSS	0.86-0.92

## Result and discussion

The removal of volatile suspended solids (VSS) as the efficiency factor haveevaluated the effects of the ration of  $\text{Fe}^{2+}$  concentration on  $\text{H}_2\text{O}_2$  concentration ( $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ), time, pH,  $\text{H}_2\text{O}_2$  concentration and current density as the effective process operation parameters. To obtain the most efficient we have investigated the operational parameter serily. The first parameter that is studied is  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ . Figure 2 shows the effect of  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  to removal of VSS. Regarding to the diagram, the removal of VSS increases sharply as  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  increases to 0.58 (optimum point) and reach its maximum in this point and is constant to about 1.015 and then decreases slightly. The second parameter is pH. It has been studied in the optimum point of  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ . Adjustment of pH has been done by 98% sulfuric acid. Figure 3 shows that the removal of VSS is constant by increasing the pH up to 3, and then starts to decrease. The maximum VSS removal (approximately 72%) was attained in  $\text{pH}=3.1$ . Oxidation efficiency essentially decreases at pH values lower than 3. Figure 4 shows the relation of VSS removal and time. The time was assessed in the maximum point of the last two parameters. According to the diagram, the VSS removal increases by time and reaches its maximum in approximately 6 hours and then is constant.

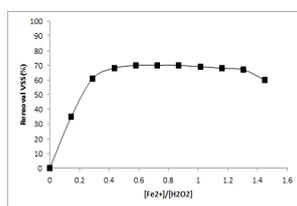


Figure 2. VSS removal and  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  relationship

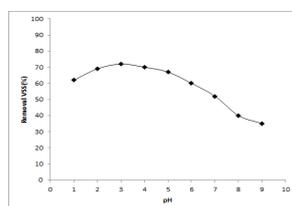


Figure 3. VSS removal and pH relationship

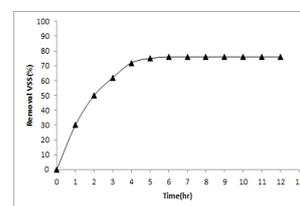


Figure 4. VSS removal and time relationship

In order to attain the best concentration of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ , we studied the effect of  $\text{H}_2\text{O}_2$  concentration on VSS removal. The optimum ratio of  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  can be attained from figure2.  $\text{Fe}^{2+}$  concentration are also resulted by determining the optimum  $\text{H}_2\text{O}_2$  concentration. The tests carried out in the most effective point of prior parameters and the results has been shown in figure 5. According to the diagram, the highest VSS removal was obtained when the  $\text{H}_2\text{O}_2$  concentration is approximately 1568mg/L. Finally, after determining the optimum point for ( $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ), detention time, pH,  $\text{H}_2\text{O}_2$  concentration, and the effect of Current density was evaluated. Current density improves the reduction of trivalent iron to divalent iron, i.e., it enhances the efficiency of Fenton process. According to figure 6, the maximum VSS removal has been reached in (650-750) mA current density. The remained  $\text{Fe}^{2+}$  concentration has also been investigated. As shawn in the figure 7, approximately (40-70)% of inserted  $[\text{Fe}^{2+}]$  adsorbed on the electrodes, (7-15)% was remained in the sludge layer and (23-45)% in the sludge liquor.

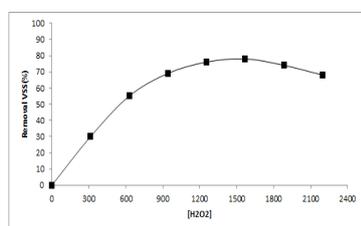


Figure 5. VSS removal and  $[\text{H}_2\text{O}_2]$  relationship

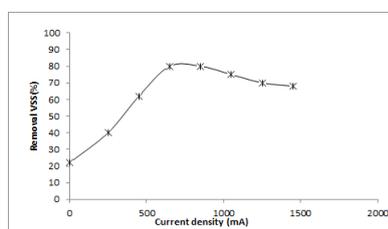


Figure 6. VSS removal and current density relationship

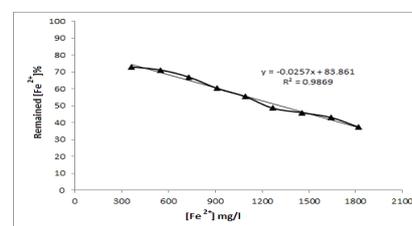


Figure 7. Remained and consumed  $[\text{Fe}^{2+}]$  relationship

Fenton and electrochemical-Fenton were compared on an equal basis. According to the figure 8, the efficiency of electrochemical-Fenton is 76%, while the efficiency of Fenton is 22%. Figure 9 shows the current density of energy consumption. By increasing the current density rate, energy consumption increases exponentially.

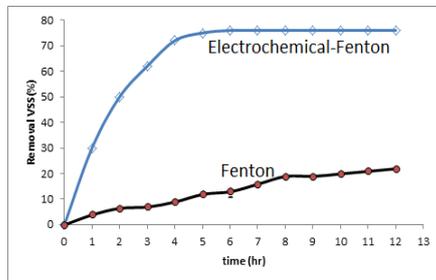


Figure 8. VSS removal efficiency of Fenton and Fenton-electrochemical regarding detention time

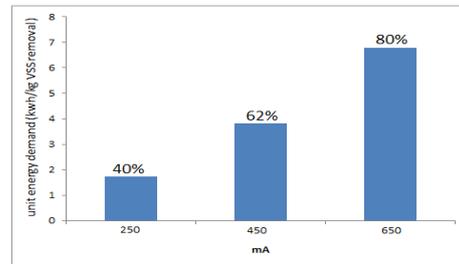


Figure 9. Current density of energy consumption in Fenton-electrochemical

## Conclusions

Even if in the recent decades many efforts have been done in order to enhance usual sludge treatment or commence novel more efficient methods, lots of researches have focused on techno-economical issues carefully. The key purpose of the researches is to eliminate the organic load of sludge and improve its quality in order to be reused in various applications like fertilizer in agriculture. In this study we have evaluated a combined Fenton-Electrochemical process with the aim of stabilizing excessive biological sludge of municipal wastewater treatment plant. For this purpose, several determining parameters have been selected and investigated in a lab-scale pilot. The results showed that the system has preserved its stability in a wide range of pH (3-7), also the organic load of the sludge decreased noticeably (maximum decreasing efficiency of the sludge was approximately 81%). Comparison of the results of Fenton or other usual systems and combined Fenton-Electrochemical process showed that the later system is appropriate and efficient method to get better quality of stabilized sludge and operational conditions.

**Keywords:** biological waste sludge, fenton– electrochemical method, organic loading reduction, wastewater treatment.

## Removal of Cd<sup>2+</sup> and Pb<sup>2+</sup> Ions from Aqueous Solutions Using Iranian Natural Zeolite and Sepiolite

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### Introduction

Industrialization and urbanization of societies have caused many environmental problems. Therefore, environmental protection has recently become highly important. Water resources are particularly of high risk of pollution from industrial waste disposal to river, surface, and ground water, and also from discharge of water to municipal waste water collection systems. These effluents usually contain a high concentration of heavy metals such as cadmium, lead, copper, and zinc which create many environmental problems due to their high toxicity.

Cadmium and lead are listed as dangerous heavy metals. These elements could contaminate soil and water resources in different ways. Remediation of soil and water contaminated with heavy metals is one of the important environmental policies in industrialized and developed countries. Many methods have been invented and used for waste water treatment such as chemical precipitation, reverse osmosis, and ion exchange, each with their own advantages and disadvantages. One of the methods developed in recent years is the use of inorganic adsorbents.

Different kinds of clay minerals such as smectite, palygorskite, sepiolite, Fe, Al and Mn hydroxides, and organic materials can be used for the sorption of heavy metals. This study has been carried out to compare the ability of Semnan zeolite and Yazd sepiolite in the removal of lead and cadmium from contaminated solutions and also to estimate the adsorption behavior of the zeolite and sepiolite minerals for cadmium and lead.

### Materials and methods

#### Preparation of mineral samples

The clinoptilolite used in this research was collected from the Siah-Zagh mine of Semnan Province and the sepiolite sample from a mine in Yazd Province. Before use, the sepiolite and zeolite samples were passed through a 0.1 mm sieve (140 mesh). Some physicochemical properties of the minerals such as pH, cation exchange capacity, and elemental analysis were determined by the use of pH meter device in saturation extract, by the method of saturation with sodium acetate, by the use of XRF, respectively. To determine the purity of minerals, the mineralogical composition of powdery zeolite and sepiolite samples was examined by an X-ray diffractometer (Philips PW-1840 model).

#### Adsorption experiments

0.5g of zeolite or sepiolite samples was mixed with 50 ml of solutions having different concentrations of Cd and Pb (0, 50, 100, 200, 400 and 600 mg/l) at pH =5. The suspensions were stirred for 24h at ambient temperature of 25±3°C and then centrifuged at 3000 rpm. The concentrations of Pb and Cd in the supernatants were determined by a GBC atomic absorption spectrometer (Savant AA). The quantity of Pb and Cd adsorbed by the minerals was calculated based on the difference between the initial and equilibrium concentrations of Pb and Cd in the solutions:

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$$C_s = \frac{(C_0 - C_e) V}{W} \quad (1)$$

where  $C_s$  is the amount of Cd or Pb sorbed per unit mass of mineral ( $\text{mg g}^{-1}$ ),  $C_0$  and  $C_e$  are the metal concentrations ( $\text{mg l}^{-1}$ ) in the initial and equilibrium solutions, respectively,  $V$  is the volume of solution added (l) and  $W$  is the air-dried mass of minerals (g).

All the experiments were performed in triplicate. The data obtained from lead and cadmium adsorption experiments were fitted to Langmuir and Freundlich equations. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent. The linear form of the Langmuir isotherm equation is represented by the following equation:

$$q = \frac{KCb}{1 + KC} \quad (2)$$

Where,  $K$  ( $\text{l mg}^{-1}$ ) reflects the relative rates of sorption and desorption at equilibrium and is thus the bonding energy coefficient,  $b$  ( $\text{mg.g}^{-1}$ ) is the maximum sorption capacity,  $q$  is the amount of Cd or Pb sorbed per unit mass of mineral ( $\text{mg.g}^{-1}$ ) and  $C$  is the concentration of Pb or Cd in the equilibrium solutions ( $\text{mg.l}^{-1}$ ).

The linear form of the Freundlich sorption isotherm is as follow:

$$\text{Log } q = \text{Log } K_f + 1/n \text{ Log } C \quad (3)$$

Where,  $C$  and  $1/n$  are the intercept and slope of the Freundlich isotherm, respectively.  $K_f$  and  $n$  are Freundlich adsorption isotherm constants being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.

## Results and discussion

The CEC and pH (1:2 water: solid ratio) values of the natural zeolite and sepiolite samples were determined 177 and  $8.5 \text{ cmol } (+) \text{ kg}^{-1}$  and 7.47 and 8.58, respectively.

### The Effect of Initial Concentration

According to the results, the effects of all the experimental factors including the type of element, initial concentration, mineral type, and their interactions were statistically significant. In other words, all the experimental parameters could influence the process of lead and cadmium sorption. When the amount of sorbents (minerals) in contact with the contaminated solutions is fixed, the number of active adsorption sites on the sorbents is fixed. However, with an increase in the initial concentration of the solutions, the amount of cadmium and lead sorbed on the mineral surfaces decreased. The coefficient of variation in the Langmuir model was between 0.91-0.97. Accordingly, both models were able to describe the data but the Langmuir model showed better fit to the adsorption data of lead and cadmium. The maximum sorption capacities ( $b$ ) of Cd and Pb onto the sepiolite and zeolite samples were found to be 50 and 52.6 and 19.2 and 29.4  $\text{mg.g}^{-1}$ , respectively.

Using the Langmuir adsorption isotherm, Ponizovsky and Tsadilas (2003) reported that the maximum adsorption capacity of lead by a Bulgarian clinoptilolite was 36  $\text{mg.g}^{-1}$ . Comparison of maximum adsorption capacity of lead in the present study (52.6  $\text{mg.g}^{-1}$ ) with that reported by Tsadilas-Ponizovsky (2003) shows the ability of Iranian sample to remove lead contamination. The Freundlich power constant ( $n$ ) for zeolite and sepiolite to adsorb lead is 2.97 and 2.94, respectively, and to adsorb cadmium is 3.6 and 4.5, respectively. Based on the Freundlich theory, the  $n$  values of 1 to 10 may indicate optimal adsorption of element on the mineral surfaces. Essington (2004) believes that the constant  $1/n$  shows the heterogeneity of adsorbing surface. When this ratio reaches zero, the heterogeneity and diversity of the adsorbing places increase and when it gets close to 1, the adsorbent surface will be homogenous. In contrast, if the unit is equivalent to one, the Freundlich isotherm becomes linear and by increasing the concentration of pollutant the uptake increases linearly. It should be noted that the maximum adsorption of an element on the sorbent could not be predicted by the Freundlich isotherm.

## Conclusion

The Langmuir model could describe the adsorption process better than the Freundlich model. The maximum adsorption capacities of Pb (II) and Cd (II) onto natural zeolite were 52.6 and 29.4  $\text{mg.g}^{-1}$ , respectively. Where, the maximum adsorption capacities of Pb and Cd onto natural sepiolite were 50 and 19.2  $\text{mg.g}^{-1}$ , respectively. The selectivity sequences based on the distribution coefficient were in lines with the values of the first hydrolysis constant of the metals. The highest  $K_f$  values were found for Pb followed by Cd. However, low  $K_f$  values were estimated for Cd. Therefore, Pb is more strongly sorbed by these minerals in comparison to Cd. The main mineral properties for the sorption of Pb and Cd onto the sepiolite and zeolite are the type of mineral, the level of pH, as well as the CEC.

Batch adsorption experiments together with our earlier results reveal that the removal of both lead and cadmium by zeolite and sepiolite involves the contribution of both adsorptions by ion exchange and precipitation.

The results of this study show that both zeolite and sepiolite can be used to prevent lead and cadmium entrance into the underground water. The results also illustrated that both adsorption and cation exchange reactions are contributing to the sorption of Cd and Pb ions onto sepiolite and zeolite. It seems that both sepiolite and zeolite minerals have a very high ability to remove Cd (II) and Pb (II) from aqueous solutions.

**Keywords:** cadmium, lead, removal, sepiolite, sorption, zeolite.

## Heavy Metals Concentration Changes during Vermicomposting of Organic Wastesq

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### Introduction

The problem of solid waste management is one of the most critical environmental issues because of rapid population and economic growth, urbanization, and industrialization. Furthermore, global attitudes are bent on accessing sustainable agriculture and conserving a clean and green environment. Vermicomposting is a process to convert organic waste by the use of earthworms to produce peat-like material which has an added advantage of possessing the potential for improving plant growth as soil conditioner. Earthworms eat, grind, and digest organic waste combined with aerobic and some anaerobic microflora converting it into stable and homogenous biofertilizer. Earthworm cast has a larger microbial population, containing plant growth hormones, higher level of soil enzymes, and also displaying desirable aesthetics. Different species of earthworms can convert various natural and anthropogenic wastes such as crop residue, dairy plant sludge, industry sludge, and cattle manure into a useful product. There is a growing interest in the use of an integrated system approach involving precomposting followed by vermicomposting to achieve specific technical objectives. This approach will be more microbially active besides being of more uniform size, hastening degradation rate, and enhancing pathogen control than either of the individual processes. It is very important having the best quality of vermicompost product to be used appropriately as a stabilized biofertilizer in agricultural applications. Good quality of vermicompost can be obtained by mixing industrial sludge with nitrogen rich material to provide higher nutrient content and an inoculum of microorganisms. Inoculation of suitable strains has been reported to hasten the rate of vermicomposting which reduce the time needed to complete the process of composting and enrichment of nutrients in the final product.

Vermicomposting of solid waste may result in an increase in heavy metal content in the final product due to mineralization of organic matter in the vermicompost obtained from various organic wastes of different chemical composition. So the organic matter mineralization and dry weight loss of the waste during the process has the effect of increasing the level of heavy metal, being the consequence of the decomposition of the waste organic matter by earthworms during vermicomposting. The application of inoculation of microorganisms such as bacteria and fungi in the substrate may accelerate the stabilization process due to biological nitrogen fixation and phosphorus solubilization. Furthermore, the heavy metals content in vermicomposts can accumulate a lot in the body of earthworms and also reduce as a result of extra water drainage. The purpose of the study were to investigate the role of inoculation of active sewage sludge in vermicomposting process to evaluate the changes of the heavy metal content possibly present in this substrate to determine potential environmental hazards. The purpose of the study was to test the technical viability of this system, initially utilizing wheat straw, and later to be employed on other substrates.

### Materials and methods

Corn residue, compost, cow dung, and cardboard with various C/N ratios were used as substrate for *Eisenia fetida*, an exotic epigeic earthworm. Corn residue was obtained from the adjacent corn farm. The compost and cow dung were prepared from the biofertilizer plant of Mashhad municipality. Cardboard was obtained from a waste collection site of a compost plant. The organic waste was washed, air-dried, and grinded.

The experiment was conducted in plastic containers with three combinations of substrate (40, 60 and 80% of corn residue and remaining the other available organic material) and four concentrations of active sewage sludge

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(0, 2000, 4000, and 6000 mg/l) in three replications. The heavy metal content of organic waste and sewage sludge prior to vermicomposting is presented in Tables 1 and 2. The organic waste was left to decompose for 30 days by the composting process and then 150 pairs of healthy adult *E. fetida*, of almost equal age were introduced into each container and vermicomposted for 40 more days. Active sewage sludge, as a source of nitrogen fixing and phosphorous solubilizing bacteria, was obtained from a wastewater treatment plant and inoculated into pre-composted organic waste at four concentration levels. During the study, the temperature in the experiment room was maintained from 20 to 25°C that is the optimum temperature range for *E. fetida*. The moisture content was changed from 60 to 70% by watering when required.

The sampling for the analysis was made on the first day (raw materials) and after stabilization of vermicomposting (70 days). Prior to microbial digestion, each sample was dried out at 80°C for 23 hours, then one gram of each was placed in a digestion tube and 10 ml of HNO<sub>3</sub> was added to analyze heavy metal. The samples were heated for 45 min at 90°C and then 8h more at 150°C until the volume was reduced to about 1 ml. The solution was filtered and transferred to a 25 ml volumetric flask, filling it by adding distilled water. The concentrations of Heavy metal viz. Magnesium (Mg), Calcium (Ca), Sodium (Na), Potassium (K), Manganese (Mn), Lead (Pb), Copper (Cu), Iron (Fe), Zink (Zn), Chromium (Cr), and Nickel (Ni) in the digested samples were determined by an atomic absorption spectrometer (AAS) using standard calibration curves. The data in this study were analyzed by using the SPSS computer software package. All the values were presented in mean ± SD (standard deviation).

## Results and discussion

There is a need to determine the heavy metal concentrations in final vermicompost, before addition to soils due to the inhibitory effect of heavy metal compounds on the growth and performance of the photosynthetic apparatus of plants. The results showed that the growth of *E. fetida* was not inhibited during vermicomposting of corn residue or by the addition of microorganism inoculants. The present study indicated that the application of sewage sludge in vermicomposting would not have any side effect as the heavy metals stayed within the limits. Although the heavy metals at low content are essential for plant growth, it is likely to have adverse effects at higher concentrations. The periodical changes of the heavy metals during vermicomposting of the organic waste considered herein are presented in Tables 4 and 5. From these results, it is evident that the earthworms were exposed to the heavy metals in all treatments and the heavy metals content was observed to increase in all the samples in the study. An increase of the heavy metals content in final vermicomposts was reported in other studies indicating mass reduction of raw materials due to decomposition of organic matter. The presence of microflora in the gut of earthworms might play an important role in this process; although an increase in total amounts of metal ions may affect bioavailability during vermicomposting. However, the decrease of heavy metals concentration in the final vermicompost was observed with an increasing percentage of corn residues in the substrate. The organic waste also lost its dry weight as CO<sub>2</sub> and moisture due to the mineralization of organic carbon. Therefore, prior to vermicompost addition to the soil, there is a need to determine the heavy metals concentration in the final biofertilizer. The heavy metals content in corn residue is lower than in the other organic substrate materials (especially compost), diluted the heavy metal content in the final product. The increase in the heavy metals in the vermicompost occurred on inoculation of active sewage sludge might be due to enhanced decomposition of organic matter by bacteria leading to an increase in the organic carbon content and dry weight reduction of the substrate. The microorganisms also reduce the bioavailability of heavy metals in substrate for earthworms by bioaccumulation (actively) and biosorption (passively); therefore the heavy metals accumulate in the substrate of the organic waste. The total heavy metal content of the final vermicompost was low in all treatments; thus its application as a biofertilizer is presumed safe in farming according to the chemical and physical specification standards of Spain, the United States of America, the European Union, and Iran.

## Conclusion

The information presented here provides a basis for the management of biodegradable waste as vermicomposting process. In the present study, vermicomposting of biodegradable organic waste and active sewage sludge was carried out where heavy metals content was higher than in the initial organic wastes. Our trials demonstrated that vermicomposting using *E. fetide* is an acceptable option for recycling and environmentally friendly disposal of corn residue. Consequently, the reproducibility of the process and the quality of the final product make it feasible to propose the use of this experimental procedure for further research entailing and facilitating a mass reduction of initial composted waste mixtures. The results also showed that after the addition of active sewage sludge in proper quantities to corn residue, it can be used as a raw material in vermicomposting. Due to adverse effects inferred that heavy metal content changes as a function of initial organic waste and active sewage sludge and comparison of the metal content in final products with stipulated standards, the final vermicompost is usable for

agricultural application as soil conditioner and/or eco-manure. It is assumed that the integrated approach employing microflora and earthworms together may be helpful in converting the waste into value added product in a short time.

**Keywords:** biodegradation, corn residue, heavy metals, sewage sludge, vermicompost.

## Anaerobic Treatment by UASB Reactor and Aerobic Biodegradability Test of Cutting Oil Sewage

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### Introduction

Water is consumed in almost all industries. Consequently the used water is turning to a waste that usually should be treated to meet the regulated standard level prior to reuse or discharge into the environment. Cutting oil wastewater is an emulsion normally comprised of 1-10% oil and the remainder water. The main functions of this oil in industry are lubrication, friction reduction, and cooling of instrument's parts. This wastewater is classified as a toxic waste according to the existence of some additive material to prevent corrosion and bacterial growth. Breakage of the emulsion and separation of the water and the oil can alone reduce more than about 90% of the aqueous phase pollution and prepare it for treatment.

The emulsion breakage can be applied with various electrolytes. According to previous researches, calcium chloride is a suitable material from an economical and technical perspective. After separation, the oil phase can be recycled or burned and the aqueous phase should be treated before disposal or reuse. A removal efficiency of about 90% doesn't satisfy the standard level for discharge to the environment.

Aerobic process usually applies in sewage with lower loading rates and anaerobic processes are more suitable for high loading rates. The design and application of up-flow anaerobic sludge blanket (UASB) reactors developed in the latter years of 1970s. The advantages of UASB reactors include lower area and volume requirement, lesser energy consumption, adjustment in shocking condition such as cutting off the substrate supply, and especially lower sludge production which all facilitate application in the industrial factories even inside of towns.

Possibility of the anaerobic biological treatment of the aqueous phase of the oil water emulsion in the UASB reactor and also aerobic biodegradation of the remained pollution as secondary treatment and the verification of Monod model are considered in this paper.

### Materials and methods

Figure 1 shows the experimental setup and Table 1 illustrates the reactor specifications.

Experimental reactor was made by Plaxy glass. Start-up sludge volume was 1.2 lit (MLSS=170 g.lit<sup>-1</sup>) which provided from a treatment plant at Tehran dairy co. Temperature during the operation retained constant at about 27±2°C which is comparable with the temperature of factories that use cutting oil. The amount of nitrogen and phosphorous in the aqueous phase is about zero; therefore, the COD/N/P ratio was controlled at 120/5/1 during the operation by the addition of K<sub>2</sub>HPO<sub>4</sub> and NH<sub>4</sub>Cl. The aqueous phase pH and the BOD/COD ratio was kept at 7 and 0.83, respectively. A Hack spectrophotometer was used to colorimetrically measure all the concentrations using analytical kits.

In this study, sewage artificially made with the cutting oil of the Tabchem factory. The oil concentration in the emulsion is 1.5% which is the common composition for use in cutting machines. The emulsion was broken by the calcium-chloride. To fulfill this task, 1 g CaCl<sub>2</sub> was added to the emulsion for each percent of oil and mixed completely thereafter. This mixture was maintained stationary for one day in decanter ampoule to separate liquid phase. The liquid phase COD is equal to 2400 mg/l which diluted with distilled water.

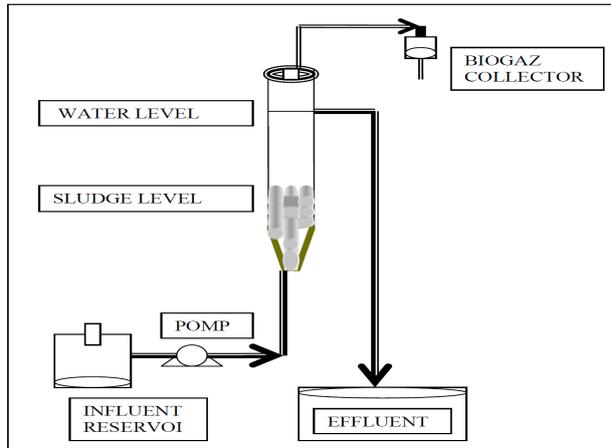


Figure 1. Experimental setup

Table 1. UASB reactor specifications

Items	Value
Total volume (lit)	4.5
Sewage volume (lit)	4
Freeboard volume (lit)	0.5
Total height (cm)	67
Liquid height (cm)	55.5
Inner diameter (cm)	9.8
Outer diameter (cm)	10.3

All the experiments were carried out in two consequent 15-day periods. First volumetric loading was  $L_v=0.69 \text{ kgCOD.m}^{-3}.\text{day}^{-1}$  with a 45 days retention time to adjust with the start-up sludge and in the second period loading was doubled to  $L_v=1.8 \text{ kgCOD.m}^{-3}.\text{day}^{-1}$  with a 15 days retention time.

Figure 2 shows the experimental setup to assess aerobic bioassay. This test is performed in a batch reactor and the achieved results can be used in the continuous operation design. Details of this unit are stated as follow:

1. Motor & mechanical mixer
2. Plaxy glass reactor, diameter and height are 15 cm
3. Baffles to break down the vortex
4. pH meter
5. DO meter
6. Air pump
7. Circular air nozzle (aquarium type)

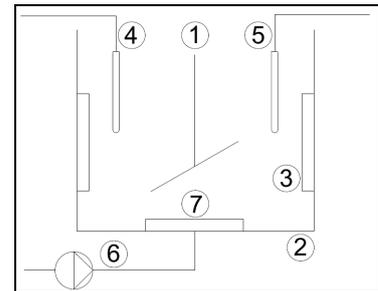


Figure 2. Experimental setup to assess aerobic biodegradability

### Discussion of results and conclusions

Figure 3 shows the COD variation of influent and effluent during t UASB reactor for two loading periods.

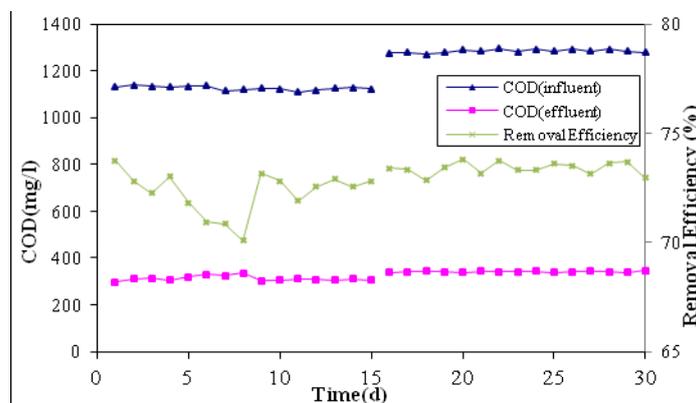


Figure 3. COD variation of influent &amp; effluent and the removal efficiency over time

As it is indicated, the average removal efficiency of the system is about 73% which implies suitable anaerobic biodegradability of the sewage. Effluent COD in the first and second period is about 290 and 350  $\text{mg.lit}^{-1}$ , respectively. An increase in the volumetric loading decreases the retention time. As it can be seen in Figure 3, the removal efficiency of the system remains constant with an increase in the loading rate. This concept

illustrates that the UASB reactor can suffer higher loading. As it was indicated in the literature, the loading rate can increase up to  $40\text{kgCOD}\cdot\text{m}^{-3}\cdot\text{day}^{-1}$  which requires preparation of such reactor condition as temperature, granule concentration, hydraulic retention time, and other relevant requirement. This reactor can comparably act as a high rate aerobic reactor with less energy consumption, smaller occupied area, and without requirement to aeration equipments.

The removal efficiency of the system is reasonable; however similar to other studies, the values are above the standard limits and it cannot be discharged to the environment without a secondary treatment. Therefore, in this paper, aerobic biodegradation assay of the residual contaminates has been performed in a batch reactor to reach the environmental standard levels. This test assesses the presence of inhibitory substances and sufficient nutrients in the effluent and can also help determine the retention time and the F/M ratio for continuous reactor design. According to the UASB effluent, COD equal to  $400\text{ mg/l}$  and initial substrate to initial biomass concentration ratio ( $S_0/X_0$ ) were set equal to 2.2 and the experimental procedure is the same as the previous step. As it can be seen in Figure 4, the residual COD reaches to about  $68\text{ mg}\cdot\text{l}^{-1}$  after 10 hr retention time which is an appropriate reduction. According to aforementioned discussion, design of an aerobic reactor with 10 hr retention time and  $S_0/X_0$  ratio equal to 2.2 is possible to treat the remained pollution in the aqueous phase of an oil water emulsion.

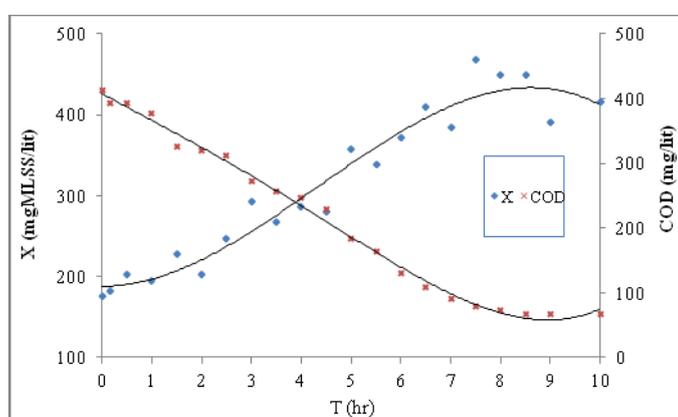


Figure 4. Biomass and substrate variation during time for  $\frac{S_0}{X_0} = 2.2$

Additionally, the measured values are in a reasonable compliance ( $\pm 5\%$ ) with the logarithmic growth phase of the Monod model according to the following equation.

$$S = S_0 - X_0 / Y_{\text{obs}} (e^{\mu_{\text{max}} \cdot t} - 1) \quad (1)$$

**Keywords:** biological treatment, cutting oil, UASB reactor, volumetric loading.

# Evaluation of Scenarios in Artificial Recharge With Treated Wastewater on the Quantity and Quality of the Shahrekord Aquifer

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## Introduction

Groundwater level is strongly falling due to dependence of agricultural, industrial, and urban water on this resource. The increasing population growth, industrialization progress, and agriculture intensification have all resulted in ever-increasing water demand for various purposes. Artificial recharge and discharge optimum management can recover the groundwater resource. The artificial recharge to the groundwater aims at augmentation of ground water reservoir by modifying the natural movement of surface water through suitable civil construction techniques.

Numerical modeling of the groundwater is an important tool in groundwater engineering practice. Modflow software as a finite difference three-dimensional model can simulate the underground flow under steady and unsteady conditions in anisotropic and non-homogeneous porous media. Modflow is designed to simulate aquifer systems in which saturated-flow conditions exist, Darcy's Law applies, the density of groundwater is constant, and the principal directions of horizontal hydraulic conductivity or transmissivity do not vary within the system. MT3D is a three-dimensional solute transport model for simulation of advection, dispersion, and chemical reactions of dissolved constituents in groundwater systems.

The groundwater of Ab-barik (Bam, Iran) was simulated to assess the artificial recharge project and the future situation of the aquifer. Modeling by Modflow show that artificial recharge has caused to recharge 12.6 mm<sup>3</sup> into the aquifer annually during 1996-1999. But despite this condition, the drawdown has been continuing on. In north-eastern of Khuzestan province (Baghmalek), the basic information of water resource including physiography, geology, sedimentation, hydrogeology, hydrochemistry, and hydrology was studied and then potential regions for artificial recharge were determined.

A program for risk management has been studied in the contamination of the groundwater resulting from leachate in landfills at Mar del Plata (Argentina). Modflow and MT3D were used to simulate the groundwater flow and contaminant transport of the uncontrolled sanitary landfill area of the city of Pocos de Caldas, Brazil.

The paper reports the modeling process of Shahrekord aquifer using Modflow and MT3D and then analyzes the quantitative and qualitative situation of aquifer after the artificial recharge scenarios.

## Material and methods

The Shahrekord plain with an area of 551 km<sup>2</sup> is located in the CHB province, Iran with 32° 07" to 32° 25" latitude and 50° 38" to 51° 10" longitude.

The Shahrekord aquifer was simulated to study the effect of artificial recharge using PMWIN 5.3 in two steps:

1. Flow treatment modeling with calibration of hydrodynamic coefficients such as hydraulic conductivity and specific yield by Modflow model.
2. Nitrate transport simulation by MT3D model, also monthly water sampling from 10 points of aquifer. The

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nitrate concentration was measured in the samples.

Figure 1 shows the situation of artificial recharge and sampling points in the Shahrekord aquifer. The model developed in duration of July 2007 to May 2008. The study year divided into some stress periods that data is changed in every period and was also defined 12 monthly stress periods with daily time steps. 10 stress periods used for calibration and two last month applied for the model verification.

The 10 scenarios of artificial recharge specified in different areas and the effect of wastewater injection on around groundwater was described.

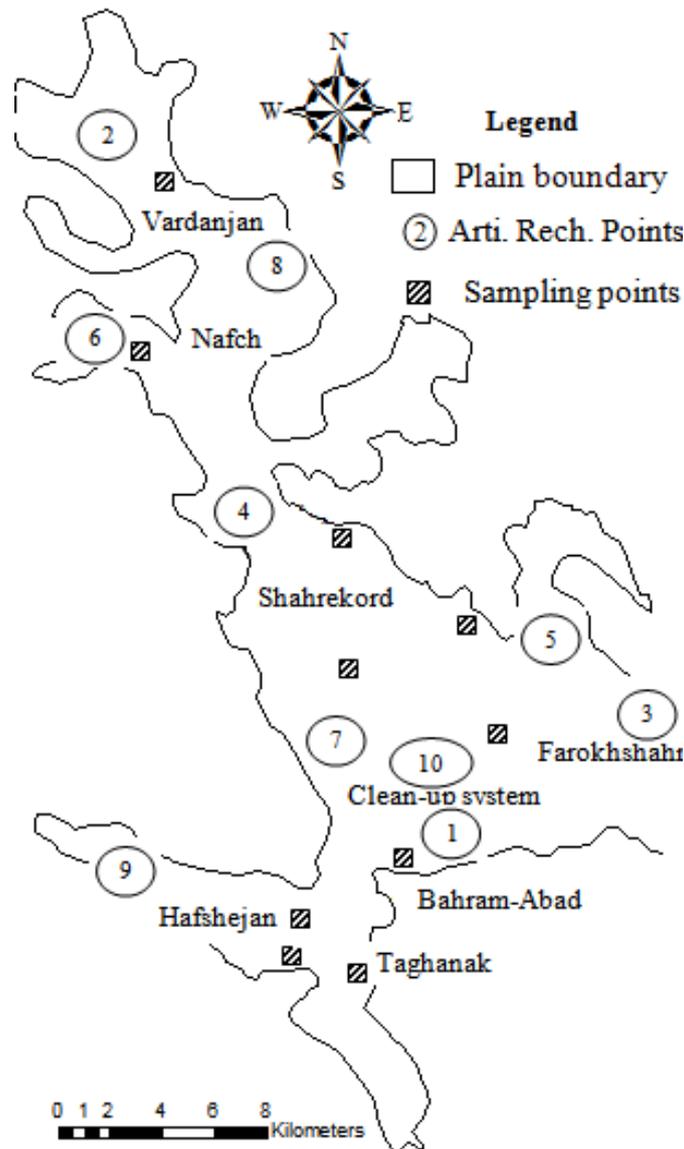


Figure 1. Position of 10 artificial recharge and sampling points of the Shahrekord aquifer

## Results and discussion

The input variables to be specified are specific yield, hydraulic conductivity, water table level, and topography of ground surface and impermeable layer. Simulation results by this model include hydraulic head and drawdown terms. Transmissivity is assumed to be calculated from hydraulic conductivity and geometrical properties. Some of the indeterminate coefficients of the aquifer were calibrated in the first step of the simulation process. Table 1 shows these values for the groundwater flow and nitrate transport models. Values mapping for the hydraulic conductivity (2-16 m/day) and specific yield (0.03-0.08) in plain surface show that the north of the aquifer has a soil with heavy texture, slower flow, and lower discharge capability in comparison to the southern parts.

**Table 1. Calibrated Parameters by the model**

Parameters	Values range
Hydraulic conductivity	2 - 16 m/day
Specific yield	0.03 - 0.08
Effective molecular diffusion coefficient	0
Longitudinal dispersivity	5
Distribution coefficient	0.0001

The first scenario of the 10 ones is the artificial recharge around the Shahrekord wastewater clean-up system. Table 2 presents the location of recharge and nitrate concentration before and after the model performance and results extractor. According to the table, nitrate concentration has increased equal to 5 mg/l in this site. The groundwater flow moved nitrate in downstream and affected the water quality about 500 m distance. It seems that this site is suitable for artificial recharge because of agricultural landuse and soil properties.

**Table 2. Nitrate concentration before and after the wastewater recharge in station 1**

UTM: 487480 , 3569210	
Water table Height	2046.88 m
Aquifer thickness	63.95 m
Hydraulic conductivity	11 m/day
Specific yield	0.062
Effective porosity	0.27
Nitrate concentration before artificial recharge	39 mgr/lit
Nitrate concentration after artificial recharge	44 mgr/lit

### Conclusion

The results show that the central and south parts of plain have a better situation for through artificial wastewater recharge. Because, injecting the water in this area increased both the water table to a radius of 6 km and the nitrate concentration to about 15 mg/lit. It predicates that the effect of nitrate plum would spread up to one kilometer from the plant in all scenarios and of course a considerable volume of water will be added to the aquifer.

### Acknowledgment

We would like to express our appreciation to CHB regional water company and Shahrekord University for financial support of this research project. The authors wish to thank CHB Water and Sewage Company for providing the useful information.

**Keywords:** artificial recharge, groundwater, nitrate and wastewater-treatment system.

## Numerical Simulation of Plume Rise in Neutral Atmospheric Stability Condition

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### Introduction

Air pollution has harmful effect on human health and the environment. Accordingly, considerable effort has been put to analyze the air pollutants. One important issue is the spatial distribution of these pollutants. Dispersion of the pollutants released from sources on the ground is mostly driven by the planetary boundary layer where turbulent flow causes mixing of the content of the stationary ground layer of atmosphere with higher moving layers and thereby clears out the pollutants rapidly. To predict the dispersion of air pollution in the atmosphere, researchers investigate the behavior of plume rise under certain conditions.

Two factors critically affect the result of the test: primary plume rise and its dispersion. In this work, we study the effective height of emission which determines the dispersion of the pollutants. The height of the plume has been subjected to semi-empirical and to more accurate numerical studies. These approaches suffer from some shortcomings. For instance, the gravitational effects and fluctuations of the wind speed are neglected. Numerical approaches are typically based on a Gaussian plume rise model so called ISC3 (published by EPA).

In this paper plume rise of emission of an air pollutant is simulated using Fluent software which allows one to input natural wind velocity profile and to consider the gravity. Another advantage of this approach lies in the usage of turbulent kinetic energy (TKE) and temperature profiles. In this work, theoretical plume rise using the ISC3 model were being calculated at first. The calculated values of  $x_f$  and  $\Delta h$  are equal to 437.85 m and 50.87m, respectively. Then, the dispersion was being simulated accordingly using Fluent and the results were compared with those of the numerical studies.

### Materials and methods

To simulate the plume rise, first a sample stack has been designed and meshed in gambit and then transferred to Fluent. Without loss of the generality of the approach, the following assumptions were made for physical factors of the chimney and weather condition. The simulation was performed in two dimensions (2D) on an area with a length of 2000 m and a height of 1000 m. The opening of the chimney was modeled at a height of 60 m and in an area of 500 m far from the entrance. The exit velocity is assumed to be 10m/s with a temperature of 450 K. The wind velocity at 10 m height is 4 m/s.

Generating a good mesh is an essential part of any CFD problem. We generated the geometry by the use of GAMBIT, the preprocessing module of the FLUENT. In the present simulation, a standard k- $\epsilon$  model is used and neutral stability condition of the atmosphere is setup using user defined function (UDF) facility of the Fluent software by defining temperature, wind, and turbulence kinetic energy (TKE) profiles at the inlet of the atmospheric boundary layer.

The wind velocity profile was obtained from AERMOD and has a logarithmic form. The vertical profile of the temperature for neutral stability condition is as follow:

$$T = -0.0098 \Delta Z + T_0 \quad (1)$$

Where,  $T$  and  $\Delta Z$  represent the temperature and the elevation gradient, respectively.

One of the significant steps is to insert the turbulence kinetic energy (TKE) profile which depends on heat transfer, momentum, and moisture in the boundary layer and the TKE obtained from the following try and error method.

In order to evaluate the effect of the gravitational acceleration on the plume rise, the simulation has been done with considering the gravitational acceleration and then the results have been compared to the results when the gravitational acceleration has been ignored.

### Results and discussions

To better compare the simulation results with the ones for semi-empirical equations, the maximum concentration and the geometric mean concentration have been averaged. The plume rise with the effect of the gravitational acceleration is shown in Figure 1. Simulation repeated with ignoring the effect of the gravitational acceleration and the results were shown in Figure 2. The maximum concentration reached its highest value approximately at 20 meter far from the stack with an effective plume height of 2.43 m when the gravitational acceleration affected the flow of the plume. But as shown in Figure 2, when gravitational acceleration has been ignored in the simulation, the plume height reached to its highest point at about 450 meter far from the stack with an effective plume height of 8.43 m.

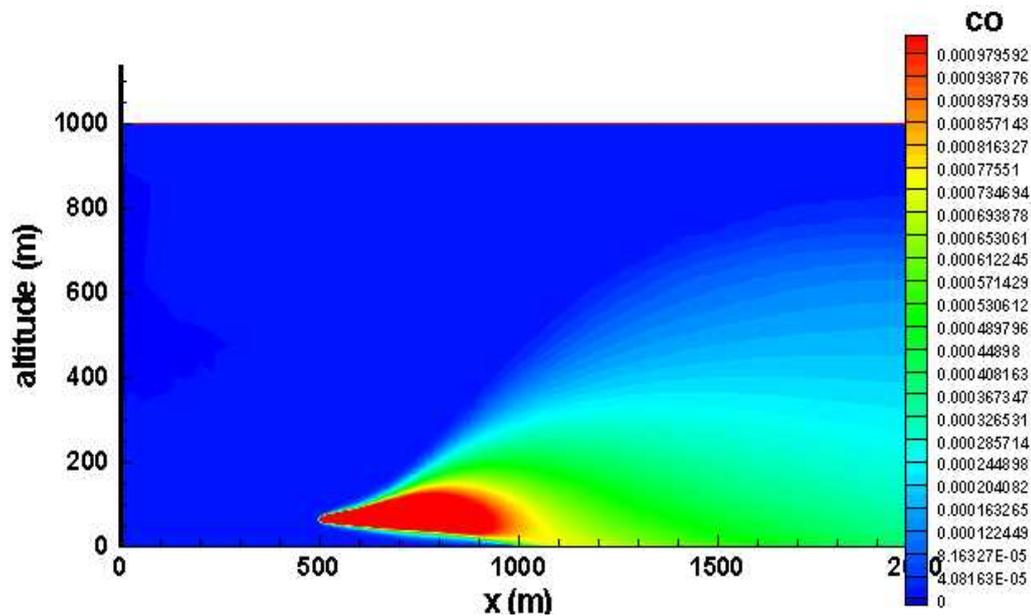


Figure 1. Plume rise in neutral atmospheric stability with the effect of gravitational acceleration

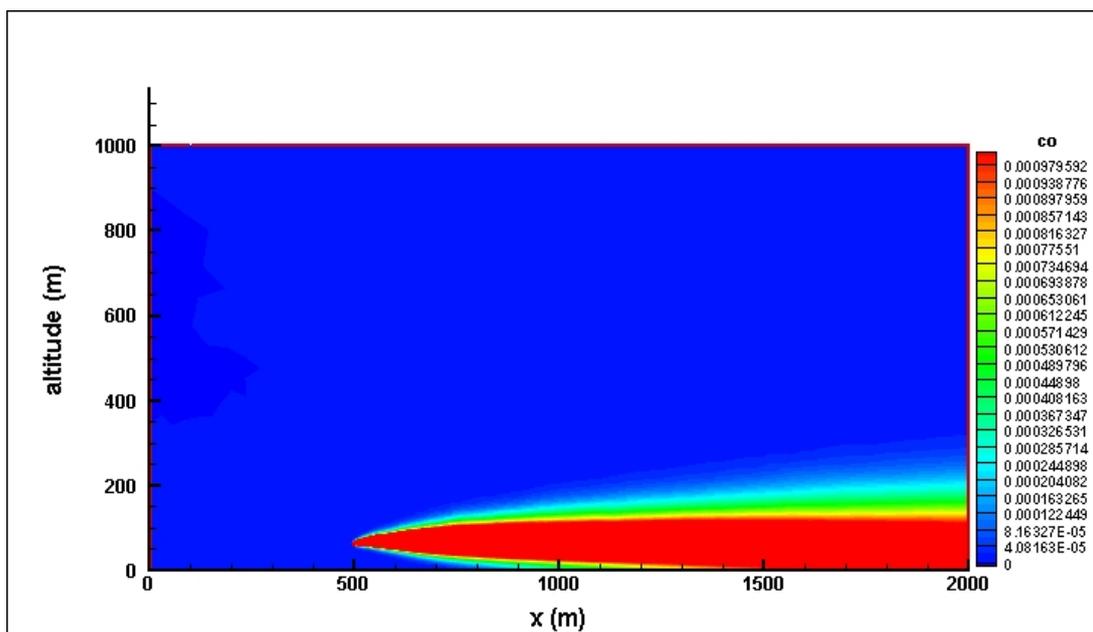


Figure 2. Plume rise in neutral atmospheric stability with ignoring the effect of gravitational acceleration

## Conclusions

The quantity of  $\Delta h$  as a function of  $x_f$  was presented in Table 1.  $\Delta h$  is obtained from the average of maximum concentration and geometric mean concentration. For the neutral atmospheric stability condition, the results give better agreement with the semi-empirical equations when the gravitational acceleration has been ignored. But, the plume rise became 2.5 times larger than the values obtained from the semi-empirical equations when the gravitational acceleration was applied. This occurs because the gravitational acceleration drawn most mass of the outlet flow; therefore, buoyancy force applied to less concentration of the outlet flow and dispersed it much more in the vertical and horizontal directions. As the presented simulation considers actual wind velocity profile, actual temperature profile, TKE profile, and gravitational acceleration effect, the results are more close to the reality.

Table 1. Comparison of different approaches for estimation of plume rise

	Semi-empirical relations	Plume rise (ignoring the effect of gravitational acceleration)	Plume rise (with the effect of gravitational acceleration)
$\Delta h$	50.87	84.53	128.94
$x_f$	437.85	437.85	437.85

**Keywords:** numerical simulation, plume rise, turbulence kinetic energy.

## An Estimation on Mortality Cost Through Air Pollution in Isfahan City

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### Introduction

Air pollution is one of the critical challenges in metropolitans around the world. According to World Health Organization (WHO), three millions people die from air pollution annually. In some studies mortality costs by air pollution was estimated. Social cost of air pollution was estimated 28990 billions Rials in Tehran city. The mortality cost by air pollution was estimated about 4.31% of GDP in Singapore. Air pollution was increased the mortality rate by 868 in Manchester city annually in 1992-98, where the social cost was estimated about £572 million.

Recently air pollution has become a serious crisis in Isfahan city in Iran. In this study the mortality cost by air pollution as a social cost was estimated in this metropolitan in 2010-2011. Also mortality rate and long run effect of air pollution were estimated.

### Material and methods

Air pollution has short run and long run effect on the mortality. Air pollution accelerate patient' death and also can shorten life expectancy of other citizens. In most empirical studies only short run effect was investigated using dose response function. In this study, an ARMAX model was used to decompose short run and long run effect of air pollution on the mortality:

$$(1+\theta_1L+\theta_2L^2)(\log(\text{MORT}) - \text{SMOOTH90}[\log(\text{MORT})]) = \alpha + (\beta_1+\beta_2L+\beta_3L^2)\text{AQI} + (\beta_4+\beta_5L+\beta_6L^2)\text{TEMP} + (1+\gamma_1L+\gamma_2L^2)e \quad (1)$$

Where, MORT is daily mortality rate, AQI is air quality index, TEMP is the average of daily temperature and  $e$  is an error term. Also seasonality effect of the mortality variable was smoothed with locally weighted least squares smoothing approach with a bandwidth of 90 days. Long run effect of AQI on the mortality rate was calculated as:

$$\text{LRE} = (\beta_1 + \beta_2 + \beta_3) / (1 + \theta_1 + \theta_2) \quad (2)$$

Also, Long run elasticity of the mortality to air pollution was calculated as:

$$\text{LREL} = [(\beta_1 + \beta_2 + \beta_3) / (1 + \theta_1 + \theta_2)] \text{AQI} \quad (3)$$

Where, AQI is the average of daily air quality index in 2010-2011. To estimate the social costs of air pollution for  $t=0$ , at first relative risk ratio was calculated:

$$\text{RRR} = \text{Exp}((\beta_1) \times \text{AQI}) \quad (4)$$

Total mortality was then divided by RRR. Difference of this figure with the total mortality yield the mortality in  $t=0$  due to air pollution. For  $t=1$ , the RRR was calculated as:

$$\text{RRR} = \text{Exp}((\beta_2 - \beta_1 \times \theta_1) \times \text{AQI}) \quad (5)$$

By multiplying mortality in  $t=0.1$  by blood money gives the approximate social cost of air pollution.

### Results and discussion

Data on the daily mortality rate, daily mean temperature, and Air Quality Index (AQI) was taken from Isfahan University of Medical Sciences, Isfahan Metrological Organization and Isfahan Environmental Protection, respectively in 2010-2011. The data are described in Table 1.

**Table 1. Descriptive statistics**

Variables	Mean	Std. dev.	Minimum	Maximum
Mortality(daily rate)	16.45	4.48	1	33
AQI index	95.13	28.6	32	240
Temperature(C)	17.22	9.73	1.20	34.9

For mortality variable the Phillips – Perron tests are able to reject the null hypothesis of unit root. The Phillips – Perron tests statistics was -781.75 for the log(MORT) variable with a five percent critical value of -29.5. The econometric results are reported in Table 2. This model includes one lagged value of AQI and a twice lagged value of temperature. Air pollution had significant effect in the mortality rate (Table 3).

**Table 2. The regression model for the mortality**

Variables	Coefficients	t-statistic	P-value
Intercept	-0.0124	-1.74	0.081
AR(1)	0.6789	5.25	0.000
TEMP(-2)	-0.0005	-2.13	0.033
AQI	0.00059	2.82	0.005
AQI(-1)	-0.00035	-1.68	0.092
MA(1)	-0.6666	-5.07	0.000
Durbin-Watson stats	2.03		
Schwartz criterion	511.30		
F	7.02(0.000)		

Source: Research Findings

### The long run and short run effects of air pollution on the mortality

The long run effect of air pollution on the mortality was calculated as (2):

$$\text{LRE} = (0.00059 - 0.00035) / (1 - 0.6789) = 0.0013$$

The Wald test showed that the long run and short run effects are significant (Table 3 and 4).

**Table 3. The long run effect of air pollution on the mortality**

Long run effect	X <sup>2</sup> Wald statistic	P-value
0.0013	110446	0.000

Source: Research Findings

**Table 4. The short run effect of air pollution on the mortality**

Short run effect	t- statistic	P-value
0.00059	2.82	0.000

Source: Research Findings

Long run elasticity of the mortality to air pollution was 0.123% that means a 1% increase in air pollution causes 0.123% increase in the daily mortality as presented in Table 5.

**Table 5. The long run elasticity of the mortality with respect to air pollution**

Long run elasticity	X <sup>2</sup> Wald statistic	P-value
0.123	110446	0.000

Source: Research Findings

### The social cost of air pollution

To estimate the annual social costs of air pollution, relative risk ratio (RRR) was calculated as Equ. 4 for  $t=0$ :

$$RRR = \text{Exp}(0.00059 * 95.13) = 1.09146$$

The total mortality (12015) was divided to this figure yield 11008 implying 1007 more deaths. Next to calculate the RRR for  $t=1$ , the lag coefficient was calculated:

$$-0.00035 + (0.00059 * 0.67898) = 0.00005$$

The relative risk ratio was calculated:

$$\text{Exp}(0.00005 * 13.95) = 1.0047$$

Dividing the total mortality (12015) by this figure yields 11958 implying 17 more deaths. Therefore, air pollution has caused 1024 deaths in 2010-11 (annually 512). Multiplying by blood money, the annual mortality cost was estimated 345 billion Rials.

### Conclusions

Air pollution has increased significantly in Isfahan city in recent years. In this study the short-run and long-run impacts of air pollution on the mortality rate was estimated in Isfahan city. For this purpose an ARMAX model was used to approximate the entire distributed lag impacts of changes in the level of air pollution on the mortality rate. Results showed that, annually, air pollution has increased the mortality rate about 8.5%. Accounting for this phenomenon the social cost has 346 billions for the residents of Isfahan. Also a 1% increase in air pollution increase 0.123% daily the mortality rate.

**Keywords:** air pollution, ARMAX model, hospital cost.

## Determination of Concentration and Sources of HCHs Isomers in Sediments of Siahrud River, Qaemshahr, Iran

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### Introduction

Along with increasing population, technology has had more developments for raising the efficiency of agricultural production. Modern agriculture must keep its production against destruction risk by pests. Then, for maintaining the production and crops against pests and diseases, large amounts of pesticides are used each year. Addition to the environment, this also threatens consumers' health. Pollution resulting from pesticides in the water due to long term effects and the high toxicity of pesticides as an environmental problem in the recent decades has been led to concerns about public health and non-target species. It should be considered that some insects and fungi will become resistant against chemical compounds over the time and therefore, farmers use ever more concentration after a while of use, so it causes to worry about toxins residues and its effects on the environment. In the present days, there are more concerns about using irregular use or misusing pesticides and its effects on the environment and human's health. This concern] needs to some extent the programs for decreasing the use of pesticides as a part of the agricultural major strategy. The lack of basic information about concentration and source of pesticides is a limitation for determining standard values that make it possible to set up the programs for decreasing the use of pesticides.

### Materials and Methods

Pesticide standards were purchased from Sigma-Aldrich Corporation and all reagents purchased from Merck Company. The Siahrud Basin with an area of over 10,070 hectares is placed in Mazandaran province in Qaemshahr city in the north of Iran, the length of this river is 5 km.



Figure 1. Geographical location of the study area and the sampling stations at Siahrud River-Iran

In this research, sampling was done in three seasons, summer (August), autumn (November) and spring (May) 2012. For selecting sites, we used land use map and identified 7 sites. In each site, 3 sediment samples have been taken by using Sediment core sampler that taken from the upper 5 cm of the sediment surface and all the samples were placed in glass containers and were transported to the laboratory in ice and were immediately put into freeze dryer for 18 hours and were screened with 63 $\mu$ m sieve. 5gr sample with 2 gr activated copper

were mixed by using diluted Nitric acid (4%) and 1 gr Sodium sulfate (activated in 120°C for 12 hours). Then 50 µl of PCNB with 5 mg/lit was added to it and then extraction was done by 100 ml from *n*-hexane and dichloromethane in 1:1 ratio for 40 minutes in the ambient temperature and in the ultrasonic bath. The upper solution of extracted soluble was separated by filter and for the second time, 60 ml of above mentioned solvent with the same ratio was added to residue sediment, and retained in the ultrasonic bath for more 40 minutes. The extracted soluble was added to the previous solutions and its volume was reached about 10 ml by rotary evaporator then to 0.5 ml by gentle stream of Nitrogen. For cleaning up, glass column was used with 30 cm height. The concerned column was filled by the following material from down to up, respectively: One piece of paper filter SS, one piece of Fiberglass, 10gr florisil that was in 90°C in the oven for one night, activated and it was semi activated with distilled water (wt/vol 6%). In the highest part in 1 cm it was put sodium sulfate and before passing, the soluble of column was pre-washed by 20ml normal hexane. Then the soluble was passed from it. Following that, the 50 ml of Solvent of diethyl ether and *n*-hexane soluble in 10:3 ratios was passed from the column and at last total collected soluble was reached volume of 0.5 ml by rotary evaporator and gentle stream of nitrogen. Its solvent was exchanged to *n*-hexane by MTBE Solvent. Finally, the last volume was reached 500 µlit. 1 µlit of this soluble was injected to GC/ECD. Identifying and measuring the residue of HCHs in the samples extracted from sediment was implemented by GC model 1000 DANI Company equipped with capillary column Optima-5 (60m length × 0.25 mm i.d × 0.25 µm film thickness). Helium and nitrogen were employed as the carrier and made up gas, respectively. The column temperature was kept in primarily temperature for 1 minute, then heated to 240°C at 10°C per minute increments, after 1 minute stop, then heated to 260°C at 1°C per minute increments and remained in this temperature for one minute, at last heated to 300°C at 10°C per minute increments, kept in this temperature for ten minutes. Identifying HCHs in sediment samples was done by comprising observed pick inhibitory time in chromatograph obtained from sample and injected standard soluble. The concentration of each pesticide was accounted by the level below pick of samples than the internal standard and putting it in Standard calibration curve equation of pesticides. It was used the ratio of the level below sample pick to the level below internal standard pick as analytical response for calculating concentration. The obtained LOD values in this method were 2 to 8 ng/lit and the recovery percent was 90% to 110%.

### Results and Discussion

$\alpha$ HCH concentration at all stations was below the limit of detection (LOD) and  $\beta$ -HCH mean concentration was between 0.024 and 0.054 µgr/gdw. The highest concentration was observed in the summer and Station 1 and was 0.089µgr/gdw. Average concentration of  $\gamma$ -HCH was between LOD and 0.109µgr/gdw. The highest concentration was 0.173µgr/gdw and observed in the summer and Station 1. The concentration of HCHs has different trend than the other pesticides in sediment along the river. For the reason of decreasing concentration of these two pesticides, it is important to consider the physicochemical characteristics of  $\beta$ -HCH and  $\gamma$ -HCH in sediment. HCHs are more polar and soluble in the water than the other organochlorine pesticides and are almost rapidly metabolized to soluble production in the water. Also increasing organic materials in sediment causes to degrade HCHs in this phase and consequently increase the amount of sediment organic material, and the amount of pesticides concentration of HCH will be decreased. The difference among isomeric components of HCH can reveal the resource of contaminant in the environment. Technical HCH contains 60-70%  $\alpha$ -HCH, 5-12%  $\beta$ -HCH, 10-15%  $\gamma$ -HCH, 6-10%  $\delta$ -HCH, but Lindane contains more than 99%  $\gamma$ -HCH. Each of HCH isomers has different physicochemical characteristics.  $\alpha$ -HCH and  $\gamma$ -HCH easily degrade in sediment due to high constant coefficient of Henry's law. It is also possible that  $\alpha$ -HCH and  $\gamma$ -HCH are altered into  $\beta$ -HCH in the environment, so  $\beta$ -HCH in most sediments, that was not currently entered technical HCH, is predominant isomer. If  $\gamma$ -HCH is predominant isomer, this may indicate new Lindane to enter the environment.

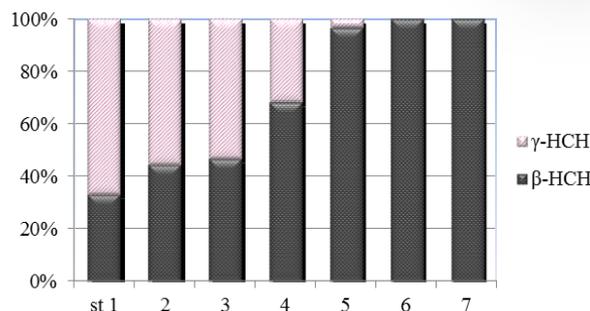


Figure 2. The differences in the percentage composition of HCH isomers in each station ( $\alpha$ -HCH in all stations were below the LOD)

Lack of  $\alpha$ -HCH in all stations is indicative of new non entry technical HCH and in the first three stations, the high percent of  $\gamma$ -HCH shows consumption of Lindane in these uses, so using Lindane is more in rice nursery. From station 4 to next stations, rapidly decreasing in isomers is indicative of non-consuming Lindane and degrading and altering it into  $\beta$ -HCH.

**Keywords:** gas chromatography, Lindane, pollution, Technical HCH.