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# Assessment of the Effect of Human and Industrial Activities on Groundwater within the City of Khoy

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## Abstract

***Background:*** *The present paper aims to study the effect of human and urban activities on the quality of groundwater within the city of Khoy in terms of heavy metals, chemical salts, and minerals from the geological formations of this region.*

***Methods:*** *Samples were provided from 32 pumping wells and the concentration of heavy metals (Cd, Cu, Mn, Pb, Zn, Fe, As, and B), the main ions (HCO3 ,SO42- ,Cl-, Mg2+,Ca2+, Na+), and NO3- were measured. In addition, TDS, EC, TH, and pH were recorded. For this purpose, graphite furnace atomic absorption, titration, and potentiometric methods were used. The obtained concentrations and values were compared with the approved standards for drinking water and agricultural water.*

***Results:*** *Concentration of most minerals, trace elements, and major ions showed dramatic increase in groundwater of eastern region of Khoy. Thematic maps produced using GIS on concentrations of heavy metals and major ions showed that the concentration of trace elements such as lead, chromium, and manganese and also sulfate and nitrate within the city of Khoy is higher than the western region of Khoy, which would be due to pollution caused by urban wastewater.*

***Conclusions:*** *Unfortunately, due to the lack of correct and principled development of sewage discharge system, especially in industrial and critical areas and discharge of domestic and industrial wastewater into the absorbent wells, the risk of groundwater contamination is strongly felt in the city of Khoy.*

**Keywords:** Groundwater, Pollution, Khoy, Chemical salts, Heavy metals.
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## Introduction

Formerly, environmental research on harmful effects of pollution and human activities were mostly focused on suburban areas and less attention was paid to environmental issues within the cities. But nowadays, given that cities and human activities are in the center of the most important environmental issues, more attention is necessary to be paid to urban and suburban environments.[1] Since groundwater is the most important supply of drinking water in many parts of the world and contamination of these sources can negatively affect human health and activities of agricultural and environmental industries, pollution of groundwater is considered as one of the most important issues of environmental engineering.[2] Unfortunately, due to the invisibility of groundwater, many people do not have enough information on the importance of groundwater and the damaging effects of environmental pollution on them.[3] In other words, domestic and industrial wastewater, urban runoff, salt waters, mine activity, industrial waste of factories, municipal wastewater, transportation, and improper disposal of solid waste are the most important factors of pollution in groundwater.[4,5] Groundwater pollution is inevitable in developing countries and the cities lacking sewage collection network.[6] In Karren areas, due to the presence of various seams in different layers and their great permeability, there is a high risk of wastewater infiltration to the groundwater.[7] Because of a semi-dry weather and low rainfall, groundwater and exploitation of them for drinking and agriculture is of special importance in the city of Khoy.

Due to overuse of chemicals in different sections of the urban and industrial activities, minor and trace elements are taken as one of the most important contaminants of groundwater. Heavy metals do not play a key role in the formation of the earth's crust and due to their extensive use in agriculture, industry, medicine, and pesticides; the presence of heavy metals is not consistent with their frequency in the earth's crust.[8] These elements can be found in the environment in various compounds such as free ions, inorganic and organic complex compounds, and metals in large-molecule organic compounds (Fats, humic acids, polysaccharides, etc.) or adsorbed by clay minerals and colloids which can bear adverse effects to public health, many of them are known to us.[9]

Despite the increasing international attention to urban environmental geochemistry, few studies have been carried out on this issue in Iran and the city of Khoy, especially by using GIS method. The present paper aims to study changes in some heavy metals such as lead, zinc, copper, cadmium, chromium, and manganese; sulfate anion, chloride, and sodium nitrate; electrical conductivity of water; and other quality parameters of groundwater within the urban area by using GIS and to determine the correlation between these elements and major cations. For this purpose, changes in concentration of above-mentioned elements and compounds in these environments, comparison of these concentrations with standard concentrations, various factors affecting these changes, and possible abnormalities occurring in different environments as a result of natural and human factors within the city of Khoy all were studied.

## Materials and Methods

Khoy is located within a vast plain enclosed by high mounts. Known as Khoy Chokhorou, this plain has an area of over 663 square kilometers. The city of Khoy is approximately situated in the central part of this region 1130 meters above sea level at 58’44” E 33’38” N (Figure 1).[10] Ghatoorchay River passes through Ghatoor region which is located near the city of Khoy.[11]

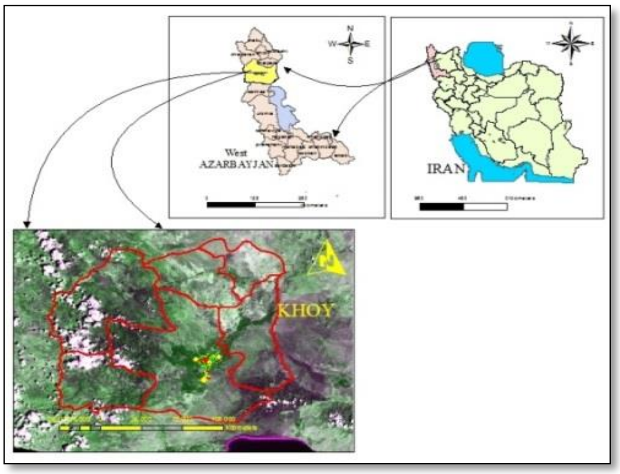


**Figure 1. Location of Khoy in West Azerbaijan Province and Iran**

During the years 2005 to 2007, the average annual precipitation in the plain of Khoy generally varied between 270 mm to 320 mm. Minimum and maximum humidity were reported in July (44.3%) and March (77.1%), respectively. Temperature also varied between -7◦C to 43◦C, although this area has experienced temperatures below -27◦C during the winter.[12] Hence, the weather of this city can be classified as semi-arid and cold.

Since the mean temperature of the warmest month, the mean annual precipitation, and the annual mean temperature during the period from 1986 till 1996 were 31.83◦C, 214.6 mm, and 13.4◦C, respectively, the climate of Khoy is drier and warmer than the climate of Urmia. The mean of frost days, the average wind speed, and the average amount of moisture during this period were also 112.2 days, 2200 m/s, and 59.36%, respectively. The slope of the plain of Khoy is from southwest to northeast and the slope of city is generally from west to east. The difference between the most western point of this city and its most eastern point is 90 meters.[13]

In terms of stratigraphy and lithology, the studied area has a diverse stratigraphic structure due to the complexity in the geological structure of geo-morphological units. Except metamorphic rock units with a lithological composition of gneisses, migmatites, and quartzite which are probably related to the Precambrian era and considered the oldest units, other rock units of the Late Precambrian are the units forming Kahar in the north of Khoy.

Mesozoic rocks consisting of igneous, sedimentary, and metamorphic rocks related to the Cretaceous are a set of colored mélange that are found in the western and southwestern parts of Khoy. The oldest rock unit of this era is made of conglomerate, representing a disruptive environment (Miocene). Upper Miocene to Pliocene teemed with deposits composed of sandstone and conglomerate with marl and shale and layers of gypsum and salt known as Upper Red Formation can be observed in a very broad area particularly in the east, southeast, and northeast of the plain of Khoy and also in the south of Ivaoghli. Sediments of the Pliocene period are a composition of conglomerate, marl, and sandstone which are distributed in the south and southeast of the plain of Khoy.

The city of Khoy is located in the central part of the plain of Khoy. Groundwater moves from southeast to northwest beneath the city of Khoy. Based on geological and geophysical studies, aquifer of groundwater of Khoy is situated in a depth of 80 meters in the west and 2-6 meters in the east and northeast. The thickness of alluvium varies between 200 meters in Dizaj areas to 50 in other areas. According to previous studies, the thickness of alluvial deposits around the city of Khoy has been reported to be approximately 200 meters. However, since the sandy part of sediments of the Pliocene period is located beneath the alluvium, the effective thickness of the alluvium could not be more than about 100 meters.[14]

Groundwater aquifer in the south of Khoy is composed of medium-grained alluvium and a layer of fine-grained sediments. Despite this variety of aquifer type in this region, Ghatoorchay alluvial fan has been reported to be made of Miocene marl (Figure 2).[15] According to the level map, the water of Khoy Plain is provided from the infiltrated water of mountains in west and southwest and also the river of Ghatoorchay.

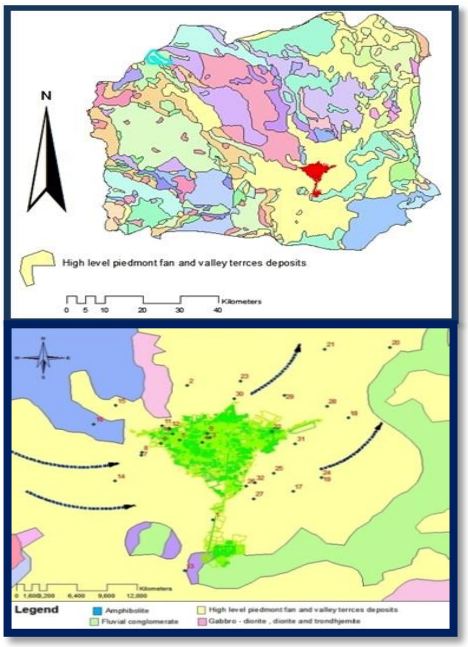


**Figure 2. Geological map of the city of Khoy, location of sampled wells, and movement path of groundwater**

There are 1094 wells in the plain of Khoy (Regional Water Authority). Since the direction of groundwater flow in the plain of Khoy is from southwest to northeast, samples were provided from pumping wells in upstream and downstream areas of the city and also within the city. So that distribution of samples in upstream, middle, and downstream areas of the aquifer is uniform. Sampling was conducted over a limited time of two weeks on 32 pumping wells (Figure 2).

Two 1.5-liter polyethylene containers were used for sampling from each point. One of the containers, after passing through the 0.45-micron filter, was purified by nitric acid to achieve a pH of less than 2.[16] This container was kept for the measurement of heavy metals and other cations. Another container of sample was prepared without acidification for measurement of anions.

pH, electrical conductivity, and water temperature were measured and recorded at the points of sampling. Geographical position of the sampling locations was recorded with GPS model GARMIN in metric system. Samples were kept at 4◦C (Standard Method) and transferred to the laboratory of Regional Water Authority of West Azerbaijan Province. Graphite atomic absorption Model Varian 220 SpectrAA and potentiometric device Model Met Rohm692 – Ion meter were used for chemical analyses (Table 1 and Table 2).

**Table 1. Analysis of chemical minerals of water at sampling points (mg/lit)**

| No | Position | EC | TDS | pH | HCo3 | Cl | SO4 | Ca | Mg | Na | K | Th |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | east city | 840 | 546 | 8.2 | 359.9 | 21.3 | 84.48 | 12 | 84 | 46 | 0 | 380 |
| 2 | east city | 1580 | 1027 | 8 | 359.9 | 106.5 | 272 | 30 | 144 | 92 | 3.9 | 675 |
| 3 | east city | 920 | 598 | 7.8 | 396.5 | 49.7 | 84.48 | 46 | 68.4 | 48.3 | 0 | 400 |
| 4 | east city | 600 | 390 | 8 | 323.3 | 17.75 | 41.6 | 30 | 55.2 | 13.8 | 0 | 305 |
| 5 | west city | 550 | 357.5 | 7.9 | 244 | 24.85 | 44.8 | 38 | 34.8 | 32.2 | 0 | 240 |
| 6 | east city | 3250 | 2112.5 | 7.8 | 170.8 | 710 | 64 | 106 | 36 | 690 | 15.6 | 415 |
| 7 | east city | 1830 | 1189.5 | 7.6 | 115.9 | 426 | 84.48 | 104 | 37.2 | 211.6 | 7.8 | 415 |
| 8 | east city | 660 | 429 | 7.9 | 140.3 | 81.65 | 46.4 | 46 | 18 | 78.2 | 0 | 190 |
| 9 | east city | 1140 | 741 | 7.8 | 353.8 | 71 | 132.16 | 50 | 72 | 75.9 | 0 | 425 |
| 10 | west city | 2180 | 1417 | 7.8 | 994.3 | 99.4 | 118.4 | 50 | 204 | 165.6 | 11.7 | 975 |
| 11 | east city | 980 | 637 | 7.9 | 103.7 | 134.9 | 74.88 | 52 | 22.8 | 98.9 | 0 | 225 |
| 12 | east city | 1680 | 1092 | 7.8 | 213.5 | 280.45 | 84.48 | 88 | 62.4 | 161 | 7.8 | 480 |
| 13 | east city | 3330 | 2164.5 | 7.9 | 134.2 | 532.5 | 544 | 138 | 82.8 | 345 | 0 | 690 |
| 14 | east city | 1770 | 1150.5 | 8.3 | 219.6 | 280.45 | 122.56 | 102 | 31.2 | 190.9 | 0 | 385 |
| 15 | east city | 1200 | 780 | 8.6 | 658.8 | 28.4 | 36.8 | 28 | 115.2 | 46 | 0 | 550 |
| 16 | west city | 890 | 578.5 | 8.7 | 244 | 35.5 | 103.36 | 40 | 48 | 57.5 | 0 | 300 |
| 17 | west city | 610 | 396.5 | 7.8 | 268.4 | 28.4 | 35.2 | 50 | 42 | 11.5 | 0 | 300 |
| 18 | west city | 810 | 526.5 | 8 | 445.3 | 21.3 | 28.8 | 24 | 87.6 | 25.3 | 0 | 425 |
| 19 | west city | 470 | 305.5 | 7.9 | 231.8 | 21.3 | 32 | 40 | 24 | 27.6 | 0 | 200 |
| 20 | east city | 1140 | 741 | 7.8 | 353.8 | 71 | 132.16 | 50 | 72 | 75.9 | 0 | 425 |
| 21 | east city | 810 | 526.5 | 7.9 | 213.5 | 71 | 65.28 | 34 | 56.4 | 55.2 | 0 | 320 |
| 22 | east city | 510 | 331.5 | 7.8 | 219.6 | 21.3 | 46.4 | 38 | 27.6 | 25.3 | 0 | 210 |
| 23 | west city | 496 | 298 | 7.9 | 243 | 19 | 27 | 50 | 28 | 12 | 1 | 240 |
| 24 | west city | 456 | 292 | 7.8 | 266 | 19 | 32 | 71 | 20 | 14 | 1 | 261 |
| 25 | west city | 538 | 344 | 7.8 | 264 | 16 | 32 | 62 | 25 | 12 | 0.9 | 259 |
| 26 | west city | 642 | 411 | 7.9 | 280 | 24 | 34 | 66.2 | 32.16 | 11 | 0.4 | 299 |
| 27 | west city | 505 | 323 | 7.7 | 281 | 13 | 19 | 57 | 28 | 10 | 0.8 | 259 |
| 28 | west city | 520 | 333 | 7.9 | 163 | 15 | 27 | 58 | 25 | 12 | 1 | 251 |
| 29 | west city | 545 | 349 | 7.8 | 253 | 23 | 35 | 54 | 34 | 12 | 0.9 | 265 |
| 30 | west city | 587 | 376 | 7.7 | 190 | 15 | 32 | 69 | 28 | 10 | 0.7 | 292 |
| 31 | west city | 571 | 365 | 7.7 | 280 | 15 | 32 | 55 | 33 | 10 | 0.7 | 277 |
| 32 | west city | 675 | 632 | 7.5 | 370 | 17 | 30 | 69 | 40 | 16 | 1 | 342 |

**Table 2. Analysis of some heavy metals in water at sampling points**

| Code | Position | NO3 | Cd | Cu | Mn | Pb | Zn | Fe | As | B |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | east city | 19 | 0.00009 | 0.0034 | 0.0005 | 0.0007 | 0.0013 | 0.0897 | 0.0007 | 3.75 |
| 3 | east city | 17 | 0.00009 | 0.0033 | 0.0005 | 0.0004 | 0.0014 | 0.093 | 0.0005 | 1.55 |
| 6 | east city | 13 | 0.0002 | 0.0068 | 0.0003 | 0.0005 | 0.0019 | 0.0545 | 0.0005 | 2.31 |
| 9 | east ity | 28 | 0.0002 | 0.0066 | 0.0003 | 0.0004 | 0.0013 | 0.1246 | 0.0006 | 2.72 |
| 10 | west city | 10 | 0.000392 | 0.00708 | 0.00415 | 0.00631 | 0.0378 | 0.05187 | 0.00197 | 3.34 |
| 12 | east city | 14 | 0.0001 | 0.009 | 0.0041 | 0.0006 | 0.0134 | 0.036 | 0.0004 | 9.179 |
| 13 | east city | 28 | 0.00099 | 0.00875 | 0.3439 | 0.01513 | 0.0466 | 0.00369 | 0.00157 | 2.84 |
| 14 | east city | 16.391 | 0.0004 | 0.0099 | 0.0007 | 0.0006 | 0.0024 | 0.1028 | 0.0004 | 2.87 |
| 21 | east city | 27 | 0.0001 | 0.0079 | 0.0002 | 0.0003 | 0.0012 | 0.1082 | 0.0002 | 3.81 |

**Table 3. Chemical analysis of groundwater samples within the city of Khoy**

| | EC(µm/cm) | TDS(mg/l) | pH | HCO3(mg/l) | Cl(mg/l) | SO4(mg/l) | Ca(mg/l) | Mg(mg/l) | Na(mg/l) | K(mg/l) | TH(mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Valid | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 |
| Mean | 1040.15 | 680.01 | 7.9031 | 292.34 | 103.45 | 80.58 | 56.47 | 53.71 | 84.14 | 1.7250 | 364.84 |
| Std. Deviation | 746.91 | 485.19 | .24690 | 168.44 | 166.21 | 98.53 | 26.94 | 40.18 | 134.01 | 3.721 | 166.55 |
| Minimum | 456.00 | 292.00 | 7.50 | 103.70 | 13.00 | 19.00 | 12.00 | 18.00 | 10.00 | .00 | 190.00 |
| Maximum | 3330.00 | 2164.50 | 8.70 | 994.30 | 710.00 | 544.00 | 138.00 | 204.00 | 690.00 | 15.60 | 975.00 |
| WHO, 2008; EPA2009 Drinking water | 2000 | 1500 | 6.8 – 8.5 | - | 250 | 250 | 200 | 150 | 175 | 12 | 500 |
| Ayers & Westcot Cultural water | 2700 | 2000 | 6.8 – 8.5 | 600 | 500 | 950 | 400 | 60 | 900 | 75 | - |

| | NO3(mg/l) | Cd(mg/l) | Cu(mg/l) | Mn(mg/l) | Pb(mg/l) | Zn(mg/l) | Fe(mg/l) | As(mg/l) | B(mg/l) |
|---|---|---|---|---|---|---|---|---|---|
| Valid | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| Mean | 19.154 | .0003 | .0070 | .0394 | .0028 | .0119 | .0738 | .0008 | 3.596 |
| Std. Deviation | 6.879 | .00029 | .00232 | .11420 | .00502 | .01774 | .03941 | .00060 | 2.208 |
| Minimum | 10.00 | .00 | .00 | .00 | .00 | .00 | .00 | .00 | 1.55 |
| Maximum | 28.00 | .00 | .01 | .34 | .02 | .05 | .12 | .00 | 9.18 |
| WHO, 2008; EPA2009Drinking water | 45 | 5 | 1000 | 50 | 50 | 5000 | 0.3 | 0.01 | 0.3 |
| Ayers & Westcot Cultural water | 600 | 10 | 200 | 200 | 50000 | 2000 | | 0.05 | 0.3 |

**Table 4. Chemical analysis of groundwater samples, emphasizing on the wells in western and eastern parts of Khoy**

| Position | | EC(µm/cm) | TDS(mg/l) | pH | HCO3(mg/l) | Cl(mg/l) | SO4(mg/l) | Ca(mg/l) | Mg(mg/l) | Na(mg/l) | K(mg/l) | TH(mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| East of city | | 17 | 17 | 17 | 17 | 17 | 17 | 17 | 17 | 17 | 17 | 17 |
| | Mean | 1436.47 | 933.70 | 7.93 | 313.61 | 176.66 | 119.68 | 59.05 | 69.95 | 142.32 | 2.759 | 439.11 |
| | Std. D | 843.69 | 548.40 | .237 | 223.67 | 203.34 | 122.55 | 35.10 | 47.94 | 164.24 | 4.92 | 197.13 |
| | Minimum | 510.00 | 331.50 | 7.60 | 103.70 | 17.75 | 36.80 | 12.00 | 18.00 | 13.80 | .00 | 190.00 |
| | Maximum | 3330.00 | 2164.50 | 8.60 | 994.30 | 710.00 | 544.00 | 138.00 | 204.00 | 690.00 | 15.60 | 975.00 |
| West of city | | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| | Mean | 591.00 | 392.50 | 7.86 | 268.23 | 20.49 | 36.27 | 53.54 | 35.30 | 18.20 | .56 | 280.66 |
| | Std. D | 122.10 | 104.10 | .260 | 66.94 | 6.03 | 19.34 | 13.50 | 16.28 | 12.96 | .433 | 52.15 |
| | Minimum | 456.00 | 292.00 | 7.50 | 163.00 | 13.00 | 19.00 | 24.00 | 20.00 | 10.00 | .00 | 200.00 |
| | Maximum | 890.00 | 632.00 | 8.70 | 445.30 | 35.50 | 103.36 | 71.00 | 87.60 | 57.50 | 1.00 | 425.00 |

Concentration of elements and compound in groundwater within the city of Khoy were presented in tables and figures and compared with permissible limit for drinking and agriculture water according to the standards of the World Health Organization (2008), America Environmental Protection Agency (2009), the European Union (1998), and Food and Agriculture Organization (1994) (Table 3). Additionally, concentrations of elements, minerals, and important factors of water quality in terms of environmental studies as input data for making the same-concentration map of these elements were selected using ArcGIS 9.3 software. Providing the geochemical maps using GIS enables us to obtain complete statistical information on the distribution of different elements and compounds in different geological environments.[17] This information helps us to optimally and correctly manage the environment of Khoy and propose proper strategies for cleaning up this environment.

According to the data of Table 3, it can be seen that the maximum concentration of minerals and trace elements measured in samples in most cases exceeds the maximum allowed for drinking water and in some cases exceeds the allowable concentration for agricultural water. However, the mean obtained from all wells of this region showed a significant difference between the averages of the eastern and western parts of Khoy which are along with the path of groundwater. In order to better intervene in analyses and disclose the intervention of municipal wastewater in the quality of groundwater, the wells were divided into two groups of western wells and eastern wells based on the path of groundwater. Accordingly, the central street of Khoy in the north-to-south direction was chosen as the imaginary line, the wells were divided into two aforesaid categories, and finally geological surveys were conducted (Figure 4). Although the average concentration of metals such as copper and zinc is less than the standard values, this indicates a serious threat to groundwater of the studied region. Concentration of ions found in evaporate formations indicates a high abnormality. For instance, the maximum concentration of sulfate anion is 2 times more than the maximum allowable concentration for drinking water. The correlation between the concentrations of major ions, trace elements, and other water quality parameters can greatly reflect the origin of these water quality factors (Table 5).

**Table 5. Correlation matrix of concentrations of major ions and trace elements existing in groundwater at sampling points**

Correlations

| | EC | TDS | pH | HCO3 | Cl | SO4 | Ca | Mg | Na | k | TH | NO3 | Cd | Cu | Mn | Pb | Zn | Fe | As | B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EC | 1 | .997** | .045 | .087 | .905** | .693** | .658** | .433* | .900** | .661** | .702** | -.194 | .682* | .322 | .603 | .643 | .593 | -.783* | .516 | -.100 |
| TDS | | 1 | .026 | .094 | .901** | .690** | .665** | .432* | .897** | .660** | .704** | -.194 | .682* | .322 | .603 | .643 | .593 | -.783* | .516 | -.100 |
| pH | | | 1 | .176 | -.087 | .100 | -.304 | .223 | -.031 | -.237 | .101 | .028 | .183 | .332 | -.004 | -.077 | -.191 | .270 | -.211 | -.132 |
| HCO3 | | | | 1 | -.273 | -.044 | -.376* | .823** | -.125 | .222 | .675** | -.470 | -.072 | -.262 | -.286 | .076 | .346 | .029 | .647 | -.122 |
| Cl | | | | | 1 | .515** | .781** | .047 | .951** | .657** | .363* | -.134 | .470 | .391 | .459 | .363 | .255 | -.636 | .084 | -.027 |
| SO4 | | | | | | 1 | .455** | .411* | .424* | .050 | .598** | .470 | .819** | .080 | .913** | .851** | .651 | -.546 | .534 | -.137 |
| Ca | | | | | | | 1 | -.216 | .644** | .401* | .188 | -.009 | .722* | .635 | .658 | .562 | .460 | -.679* | .196 | .056 |
| Mg | | | | | | | | 1 | .132 | .338 | .918** | -.279 | .088 | -.346 | -.002 | .309 | .503 | -.185 | .758* | -.005 |
| Na | | | | | | | | | 1 | .739** | .394* | -.274 | .316 | .242 | .260 | .231 | .168 | -.520 | .115 | -.158 |
| k | | | | | | | | | | 1 | .502** | -.740* | -.162 | .005 | -.265 | -.079 | .137 | -.419 | .246 | .199 |
| TH | | | | | | | | | | | 1 | -.312 | .423 | -.095 | .295 | .594 | .762* | -.510 | .923** | .020 |
| NO3 | | | | | | | | | | | | 1 | .290 | .076 | .475 | .265 | -.004 | .226 | -.143 | -.205 |
| Cd | | | | | | | | | | | | | 1 | .464 | .908** | .936** | .814** | -.623 | .665 | -.226 |
| Cu | | | | | | | | | | | | | | 1 | .292 | .286 | .340 | -.314 | .049 | .379 |
| Mn | | | | | | | | | | | | | | | 1 | .927** | .741* | -.675* | .515 | -.119 |
| Pb | | | | | | | | | | | | | | | | 1 | .925** | -.736* | .790* | -.133 |
| Zn | | | | | | | | | | | | | | | | | 1 | -.790* | .896** | .071 |
| Fe | | | | | | | | | | | | | | | | | | 1 | -.576 | -.320 |
| As | | | | | | | | | | | | | | | | | | | 1 | -.170 |
| B | | | | | | | | | | | | | | | | | | | | 1 |

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

In order to study the spatial variation of concentrations of elements in groundwater of Khoy, geochemical maps were provided using GIS technology. These maps can fully and clearly show the statistical distribution and correlation between the measured concentrations of elements and compounds in this range. Areas with high abnormality can be also identified by using these maps.

Given that the city of Khoy is situated on terrace deposits layers and old high foothill alluvial fans, it is expected in the present study that in the case of no impact of urban sewage on the quality of groundwater, geochemical maps with the same statistical distribution would be obtained. However, such a thing was not observed in provided maps, all indicating the impact of wastewater on the quality of groundwater.

For closer scrutiny and also in order to realize the issue, case study of a number of chemical parameters was done. Electrical conductivity (EC) is a general parameter that gives us a general attitude towards the status of water. To investigate the changes in EC of groundwater within the city of Khoy, concentrations of major ions in water were plotted against EC using the results of analysis in order to estimate the probable source of the minerals increasing the EC. As shown in Table 5, correlation coefficient of EC in the aquifer with chloride and sodium ions is high (more than 0.905). This comparison between the wells of the western and the eastern parts of Khoy also shows higher affectability (Figure 3).

Referring the geochemical maps of electrical conductivity, it can be observed that the passage of Ghatoorchay River through marl and shale formations belonging to the Miocene increases the value of EC. However, abnormalities in several points of downstream of the city are indicative of long-term leakage of sewage into groundwater. After further field surveys, it was noticed that the existence of sand facilities, asphalt factory, the place of temporary storage of municipal waste is quite evident in the surrounding and upstream of two points of 23 and 26. This indicates the leakage of leachate, heavy metals, and other minerals into the groundwater. In order to confirm the presence of minerals and heavy metals, geochemical maps were prepared which are shown in Figure 4.

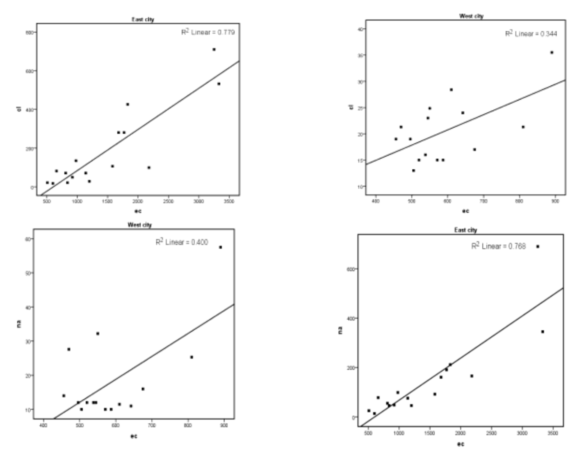

**Figure 3. Correlation of electrical conductivity (EC) with sodium and chloride ions in the western and the eastern parts of Khoy**

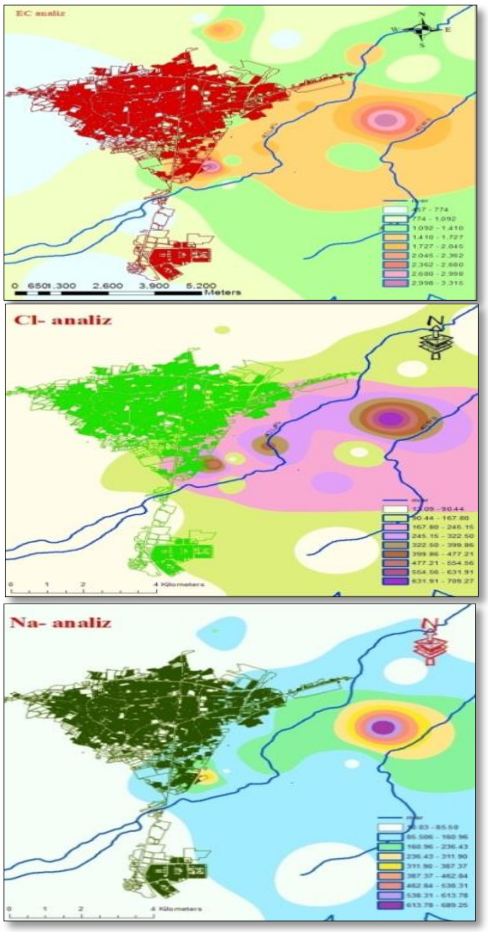


**Figure 4. Geochemical map of EC, Cl, and Na within the studied area**

In the present study, correlation matrix was used to determine the relationship of heavy metals with each other (Table 5). According to Table 5, there is a high correlation between manganese, lead, cadmium, and zinc. There is also a high correlation between iron and other metals. Arsenic shows a very good correlation with zinc. Generally, it was observed on the provided parallel maps that the highest levels of pollution caused by heavy metals were related to the southern part of Khoy that is the place to pile annual municipal waste, facilities of automobile repair, the old slaughterhouse, and salt storage for winter.

Cadmium concentration in the entire studied area varies between 0.1 and 0.2 micrograms per liter, while it is in the range of 0.99 to 0.4 in the south, east, and northeast of the city. According to correlation coefficients, this increase is due to the dissolution of certain minerals in geological formations beneath the city of Khoy. Among the heavy metals studied, cadmium has the greatest tendency to be situated in the minerals containing calcium.[18] However, sudden increase of cadmium in two southern and eastern points of the city as a result of sand facilities, storage of garbage, small factories, and entry of industrial wastewater in this area is noteworthy (Figure 5).

Increase in lead concentration in the south of the city is quite tangible (Figure 6). Maximum concentration of lead in the south of the city is more than 15 micrograms per liter which is due to the problematic well adjacent to the place of piling up the municipal garbage. This can be attributed to the presence of lead in wastewater and leachate and also the urban motor facilities.

Manganese is also more concentrated in the southern area of the city. Weak correlation of this element with major cations shows that this element has human source and be resulted from the sewage and leachate piled up in the southern part of the city (Figure 7).

Increased concentration of arsenic in the south and the east of Khoy clearly demonstrate the severe pollution of groundwater resulting from the activities of industries and factories and uncontrolled expansion of various industries in the east of the city of Khoy. As already mentioned, filed observations in the east of Khoy in Hamidabad region revealed that activity of industries is rapidly growing and the effluent from these industrial activities, due to not observing the principles of effluent disposal, enters underground wells and finally underwater (Figure 8).

The study of parallel maps of nitrate ion shows a high concentration of this ion in the east of the city, as this distribution records maximum and higher figures. The points which demonstrate high abnormality include the southern region in the well adjacent to the place of piling up the garbage, the east of the city, and at the refinery of wastewater of Khoy (Figure 9).

Other geochemical maps showed that concentration of bicarbonate ion has an increasing trend in the center of city. This can be attributed to the entry of wastewater rich in organic matter into the groundwater. As a result of decomposition of organic matter, carbon dioxide ($CO2$) is produced and causes the production of bicarbonate ion in water, increasing the concentration of this ion. Based on geochemical maps, the highest concentration of calcium and bicarbonate ions in this region was 138 ml/lit and 924 ml/lit, respectively. Concentration of other ions accumulated in evaporite sediments shows an increasing trend from west to east which is not something unexpected. Dissolution of minerals such as calcium and magnesium sulfates and halite is the cause of increased concentration of major ions including sulfate, chloride, magnesium, sodium, and calcium. Abnormalities in two points of the studied area are due to the leakage of wastewater and sewage from industrial activities and unprincipled disposal of garbage in the east and south of Khoy (Figure 10).

## Discussion

Unfortunately, due to the lack of correct and principled development of sewage discharge system, especially in industrial and critical areas and discharge of domestic and industrial wastewater into the absorbent wells, the risk of groundwater contamination is strongly felt in the city of Khoy. The use of absorbent wells system for disposal of municipal wastewater has greatly increased the level of groundwater in the eastern part of the city and posed many problems in terms

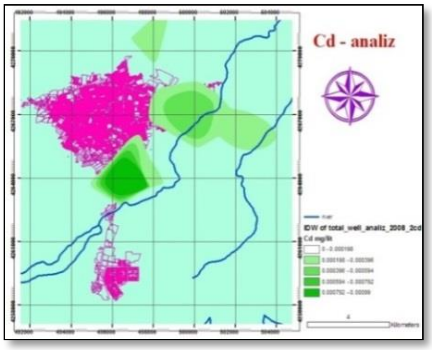


**Figure 5. Geochemical map of cadmium in the studied range**

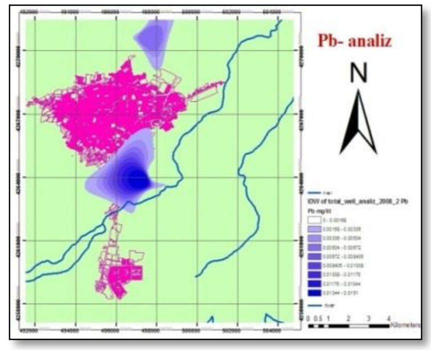


**Figure 6. Geochemical map of lead in the studied range**

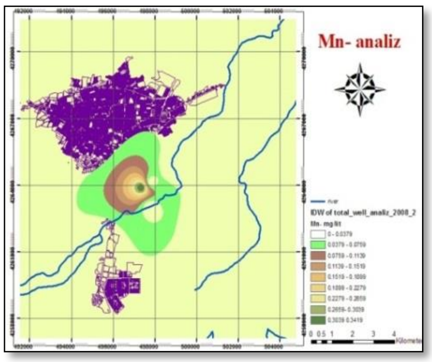


**Figure 7. Geochemical map of manganese in the studied range**

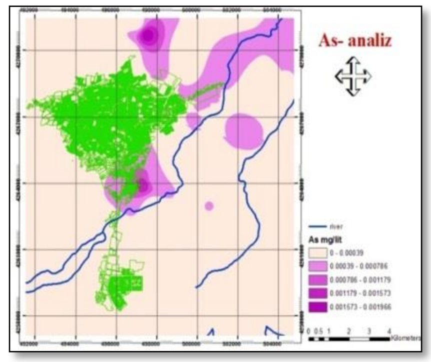


**Figure 8. Geochemical map of arsenic in the studied range**

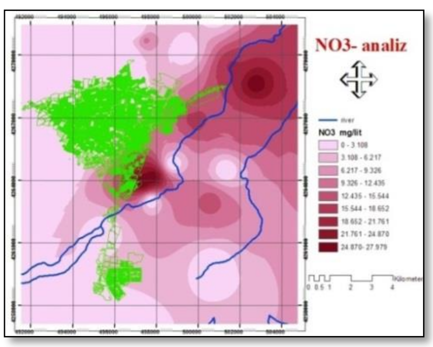


**Figure 9. Geochemical map of nitrate ion in the studied range**

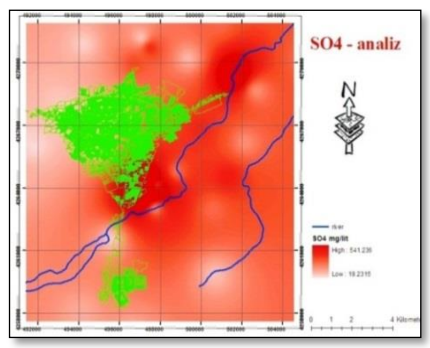


**Figure 10. Geochemical map of sulfate ion in the studied range**

of pollution transport. Because of variation in manufacturing activities, industrial wastewater in the eastern part of Khoy is highly diverse and, due to the lack of wastewater and surface sewage collection system, the quality of groundwater in the east of Khoy is severely affected. On the other hand, since the location of garbage pileup is the south of the city of Khoy which has been the place of garbage disposal and the garbage of previous are piled up there and also the existence of technical facilities associate to the municipality such as repair shops and parking of heavy machinery, the old slaughterhouse, and other activities, high concentrations of heavy metals in groundwater of this region is something completely obvious. Although the maximum concentrations of some metals do not exceed the maximum permitted by the World Health Organization, the horizontal or vertical migration of toxic trace elements in soil depends on surface water runoff in gutters and the soil type. On the other hand, migration of these elements with soil properties such as pH, structures of the soil horizons, size and composition of soil grains, absorption ability, frequency of microorganisms, the solubility of their various chemical forms, and the ability to absorb elements with colloids like clays, manganese and iron oxides, and organic compounds which are effective in absorbing these toxic elements and natural treating and clearing of waters cannot be neglected (19). Hence, movement of these elements is indicative of expansion of pollution within the soils of that region.

Given the soils of the studied area are sedimentary and groundwater can easily move through it and since most heavy metals are as cations with two positive charges, increased pH reduces their mobility and increases their absorption by soil colloids.[20] Analysis of data revealed that certain geological formations including evaporite sediments (salt and gypsum) are the most important source of chloride and sodium sulfate pollution. Disposal of household garbage and discharge of effluent of sewage refinery of Khoy into the river of Ghatoorchay are effective in increased concentration of nitrate, sodium, and chloride. Surface runoffs of alleys and streets and sewage of small factories which are secretly discharged into groundwater aquifer through absorbent wells can increase the concentration of toxic trace elements.

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## Conflict of Interest:

The authors declared that they have no conflict of interest.

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