**Original Research** 

# Assessing Pollution Risk in Ardabil Aquifer Groundwater of Iran with Arsenic and Nitrate Using the SINTACS Model

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#### Abstract

Groundwater vulnerability assessment is a general method for studying groundwater pollution. This study aimed to assess the pollution risk of groundwater with nitrate and arsenic. Risk is comprised of two parts: calculation of occurrence probability map and composition of occurrence probability map with groundwater vulnerability model. To draw up a groundwater vulnerability map, the SINTACS model was used. The correlation of the model with nitrate and arsenic concentrations was investigated. The correlation coefficients of the SINTACS model with nitrate and arsenic were r = 0.70 and r = 0.85, respectively. According to sensitivity analysis, we concluded that the SINTACS model had the least sensitivity to hydraulic conductivity. To prepare the occurrence probability map, nitrate and arsenic concentrations were combined separately with the groundwater recharge potential model. Finally, the risk map was prepared by combining the occurrence probability map and groundwater vulnerability with the SINTACS model. The results revealed that 14.72% of the study area had a high risk of nitrate and 35.33% had a high risk of arsenic. The areas with high pollution risk are those which are considered agricultural lands based on the land use map.

Keywords: arsenic, nitrate, groundwater pollution, risk assessment, SINTACS

#### Introduction

Groundwater is one of the main resources of water supply and plays an important role in human health and many aquatic ecosystems [1, 2]. The sustainability of groundwater use is one of the biggest concerns

of policymakers [3] and is at risk of pollution due to agricultural activities, industrial development, urbanization, and mineral activities. In arid and semiarid regions, in most cases, water is a limiting factor, and assessment and appropriateness of groundwater resources for various uses in these areas are very important [4]. In arid climates, increasing population and economic activities along with changes in quality, quantity, and distribution of groundwater resources threaten these resources [5]. Thus, the awareness of

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changes in groundwater quality plays a significant role in planning and managing water resources. Usually, aquifers are highly permeable, resulting in high sensitivity to surface pollutants.

Arsenic is a toxic semi-metal that has spread to the environment. Arsenic may have a natural or human origin, including industrial wastewater discharge, fossil fuels, and the use of herbicides and pesticides in agriculture. This element is known as the first carcinogen by the International Agency for Research on Cancer [6]. The use of arsenic-polluted water is one of the main concerns around the world [7].

Nitrate is a very important agricultural fertilizer and is advantageous in terms of its sustainability and non-loss of nitrogen in the atmosphere. Nitrate is obtained from the oxidation of nitrogenous compounds that becomes nitrite in the human body and causes methemoglobinemia [8].

After groundwater pollution, it is impossible to return to its original quality. Preventing groundwater pollution is essential for protecting groundwater resources. For this purpose, first the areas with high sensitivity should be identified. The concept of groundwater vulnerability was introduced by Margat as the possibility of penetration and spread of groundwater pollution [9]. The vulnerability is divided into two groups: 1) an inherent vulnerability that depends on hydrogeological characteristics of the aquifer, and 2) specific vulnerability that evaluates vulnerability in specific pollution or a group of pollutants. There are three general ways to assess the vulnerability of groundwater pollution, namely statistical methods, process-centered simulation models, and GIS-based overlay index methods. The overlay indices are relatively simple methods that are used globally [10], since they are cheap compared to other methods and directly achieve the goal, and the data they use are available or can be estimated, and their final results can be easily described. These methods are based on

hydrogeological characteristics that affect groundwater pollution [11]. In recent years, many methods have been developed for assessing vulnerability based on the overlay indices, which are DRASTIC [12], GOD [13], AVI [14], and SINTACS [15]. In the overlay methods, the vulnerability of an aquifer is estimated based on the transmission of pollution from the ground to the layer. These methods differ in using the type and number of parameters and finally record a numerical index or score for each characteristic. In terms of the sources of overlay indices, in this study the SINTACS model was selected due to its high accuracy, efficiency, and multiplicity of information layers used to assess the pollution potential of the Ardabil aquifer. It is believed that in this case, the effect of errors and uncertainties of a parameter is limited in the final output. Many previous researchers used this index to estimate vulnerability [16-19]. In the next step, arsenic and nitrate concentrations in groundwater were combined with the layers of groundwater recharge potential model, and an occurrence probability map was prepared. The final risk map was obtained via combining a groundwater vulnerability model and occurrence probability map. In this study, the final goal is to assess pollution risk of the groundwater with arsenic and nitrate as the most important parameters in pollution which cause many problems in human body.

#### **Materials and Methods**

# Study Area

The study area of Ardabil aquifer is located in Ardebil Province, which includes the cities of Ardebil and Namin with an area of 1153 km<sup>2</sup> in the northwest of the Iran Plateau. This aquifer is located at 37.45° to 39.42° north latitude and 47.30° to 48.55° east longitude (Fig. 1). A total of 76 wells were selected in the study



Fig. 1. Location of the study area to monitor vulnerability of Ardabil aquifer

area in November 2011. Ardabil Province has four Mediterranean climates: warm, moderate, cold, and temperate. This province is one of the coldest areas of Iran, which is cold 4 to 8 months of a year. On average, the rain level in the province varies between 250 and 600 mm. Spring and winter are the two rainy seasons of the area, and a large amount rain occurs in spring. The mean temperature of the province is about 7°C. The aquifer is an open and semi-under-pressure aquifer, and its main recharge source is rain. The geomorphologic maps show that some parts of the study area include geological formations of basalt and andesite. Basalt is a hard rock belonging to the group of igneous rocks and is the surviving volcanic activity. Therefore, due to its structure, it is expected that water penetration to basalt will be difficult. The conglomerate is a sedimentary rock that is formed due to the cementation of rocky parts to the size of the pebble and gravel, which include the northern parts of the study area. However the study area is mainly of alluvial type and highly permeable.

#### Pollution Vulnerability Evaluation Methods

#### SINTACS Model

The SINTACS model was developed by Civita [15] to assess the relative vulnerability of groundwater pollution using seven hydrogeological parameters derived from the DRASTIC model. The layers of this model are the same as the layers of the DRASTIC model, which differ only in rating and weighting the layers. This model includes seven hydrogeological parameters affecting groundwater pollution such as groundwater level, net recharge, aquifer media, soil texture, topography, vadose zone, and hydraulic conductivity, which are integrally analyzed and then processed through geographic information system (GIS). The SINTACS model has more flexibility than the DRASTIC model, in which specific weights of the layers are between 1 and 5, and the ratings are between 1 and 10.

To prepare the groundwater level layer, wells' log data were used. In general, in the southern areas of Ardabil aquifer, the groundwater level is higher than it is in the northern parts.

Net recharge layers were prepared using Piscopo's [20] method. In preparing this layer, rainfall is the most affecting factor due to being the main source of groundwater supply. Via combining the rainfall rated map with rated maps of soil and slope, the net recharge of the aquifer is achieved. In Ardabil aquifer, the net recharge is in a middle position since the rainfall range is less than 500 mm in the mentioned year, and according to Piscopo's method, its rate is one.

The observation and utilization logs were used to prepare a vadose zone layer. The material in the western and southern areas of Ardabil aquifer is a characteristic of coarse grain sediment, which has high permeability and is effective in the transmission of most pollutants. Soil media includes the upper portion of the vadose zone that continues to penetrate to the roots of the plants or the activity of organic organisms. The wells' log data were used to prepare this layer. Finally, after rating the desired layer, we used an inverse distance weighting method (IDW) to prepare the layer. Soil media in most parts of the area is coarse grain, and some parts of the northern, central, and southern areas include a combination of soil, clay, sand, and silt.

The aquifer media is the aquifer composition. To prepare the aquifer media layer, wells' log data were used in the area.

To provide a hydraulic conductivity layer, the statistics of wells' log and Todd and Mayes's table [21] were used. Very few northern and western parts of the area are rated to be average, and the western parts of the areas are rated to be very high. Highly rated areas are indicative of coarse grain sediment, in which the material transfer rate is high.

The digital elevation model (DEM) was used to prepare the topographic layer. Previous studies showed that in the border areas of the study area the slope is more (2-12%), and very small parts of the south (0.5% of the study area) have a slope of more than 12%.

# Validation of Model with Nitrate and Arsenic Concentrations

**Nitrate** is essential for producing crops, the source of which is nitrogen in the soil or nitrogen fertilizers [22]. Nitrogen pollution in groundwater is one of the most important factors in reducing water quality [8]. In recent decades, the use of chemical fertilizers containing nitrogen, which are used extensively for agriculture, has led to an increase in nitrate concentration in surface and groundwater [23]. The permitted rate of nitrate in groundwater is 50 mg/L [24, 25]. Due to the importance of nitrate in groundwater, in many studies nitrate concentration has been used to validate models that examine vulnerability or pollution risk of groundwater [26, 27]. Therefore, to validate the SINTACS model, nitrate concentration in groundwater was used.

Arsenic is an element that is very common in soils and aquatic media and has become an important issue in the field of environment and agriculture due to its high toxicity. Different standards have been presented for this element [28]. According to WHO [24], the standard value of this element is 0.01 mg/L. Originally, Arsenic can be found in various natural processes such as erosion of bedrock or volcanic material [29], hot water springs [30], and human activities such as adding arsenic-containing pesticide and herbicides [31]. The use of arsenic in the long run can lead to several nervous, cardiovascular, respiratory, liver, and skin diseases and cancers in humans [32]. Sidibe and Xueyu used heavy metal concentrations to validate their vulnerability model (DRASTIC) [27].

#### Sensitivity Analysis of SINTACS Model

Pollution vulnerability models are very sensitive to the weight and rate of input parameters [33]. Sensitivity analysis is a method in which input parameters of models are changed, and the system response is assessed against these changes. Then the sensitivity of the model to each parameter is determined. The effect of each parameter used in the SINTACS model was assessed using sensitivity analysis through the map removal method, where first each parameter was separately removed from the calculation, and then the most effective parameter in groundwater pollution was determined in the study area. The sensitivity of the model via map removal method [34] is presented using equation (1):

$$\mathbf{S} = \left( |\mathbf{V} / \mathbf{N} - \mathbf{V}' / \mathbf{n} | / \mathbf{V} \right) \times 100 \tag{1}$$

...where S is the sensitivity measure expressed in terms of variation index, V and V' are the unperturbed and the perturbed vulnerability indicators, respectively, and N and n are the number of data layers used to compute V and V'. The actual vulnerability index obtained using all seven parameters was considered as an unperturbed vulnerability, while the vulnerability computed using a lower number of data layers was considered to be a perturbed one.

Many researchers have analyzed sensitivity using the map removal method to determine the importance of layers in the SINTACS model, then remove the least important layer, and add other layers such as land use or fault [16, 27, 35-37].

# Creation of Pollution Occurrence Probability Map

The selected layers for this section have a significant effect on the transmission of pollution and are known as effective layers in groundwater recharge potential, as described below.

#### Inputs

Rainfall is often referred to as the predominant resource of groundwater supply in all climatic zones [38]. Obviously, in the case of more rainfall, it is expected that the supply of groundwater is higher and vice versa. The data of this layer were obtained from the statistics of meteorology stations of Ardabil Province in 2011 (Fig. 2). According to this figure, precipitation is within the range of 277 to 535 mm. The area where rainfall is greater is closer to the Caspian Sea, and it seems that the precipitation is affected by the proximity of these areas to the Caspian Sea.

Geomorphology represents important geomorphic units, landforms, and ground roughness. In this study, a 1:100000 geologic map of Ardabil Province was used



Fig. 2. Rainfall map of Ardabil Province.

to prepare the geomorphology layer. North, south, and east of the study area have basalt and andesine formations that have very low permeability. In the northern areas, there are conglomerate formations consisting of sedimentary rocks. Alluvial formations are present in most of the areas where the percentage of its permeability is high.

Faults underground fractures and can be mentioned as secondary porosity [39], which are among the factors affecting surface water penetration and its accumulation underground as well as conducting them based on the gap direction [40]. In this study, fault density was identified using a fault map of the country. The fault density is higher in the border areas of the plain, especially in the southern areas, and is lower in the central and other areas.

River density indicates the length of drainage on the surface [41]. This means that areas with lower drainage densities are suitable for groundwater recharge [42]. Via examining this layer, it was found that, in general, river density is low in this area (Fig. 1).

Soil texture determines the amount of penetration or runoff and hence has a great impact on the transmission of groundwater pollution.

Digital elevation model (DEM): In highlands, water flows as runoff on the surface rather than penetrating into the ground surface. However, in flattened areas, if soil conditions are desired, water penetrates deep into the soil and groundwater is stored there. The elevation changes in the border areas are between 1350 and 1721 m; however, the central areas are flattened, where the changes in elevation are between 1262 and 1350 m (Fig. 1).

The slope can be considered as a surface index for identifying groundwater conditions and is an alternative to the surface runoff velocity and deep penetration.

# Occurrence Probability Map

To show the pollution risk of groundwater, nitrate and arsenic concentrations in groundwater of Ardabil

aquifer were used in November 2011 and were separately combined with groundwater recharge layers. Nitrate concentrations higher than 50 mg/L and arsenic concentrations higher than 0.01 mg/L are considered contaminated areas.

In this study, a pollution risk map consisting of a combination of the layers of recharge potential model (including rainfall, geomorphology, fault density, river density, soil, DEM, and slope) are effective in the transmission of pollution by water to the aquifer. In this case, parameters of nitrate and arsenic are prepared. In recent years, various studies have been conducted to assess the pollution risk of groundwater via vulnerability models. Using nitrate and DRASTIC model layers, Zhang et al. [43] assessed pollution risk of groundwater under different scenarios of fertilization and irrigation. Pisciotta et al. [18] conducted a comparative study of nitrate risk assessment in groundwater using DRASTIC and SINTACS models and concluded that the latter provided better results.

#### **Results and Discussion**

# The Results of Groundwater Vulnerability Assessment

# Sensitivity Analysis of Model via Map Removal Method

The results of sensitivity analysis of the SINTACS model are presented in Table 1. As Table 1 shows, SINTACS had the least sensitivity to hydraulic conductivity with a mean value of S for this parameter of 0.007. In this study, the most important layer is the vadose zone, with a mean value of S of 1.83, and the model has the highest sensitivity to this layer.

# The Results of Groundwater Pollution Vulnerability by SINTACS Model

The groundwater vulnerability map was analyzed using SINTACS (Fig. 3).

Studying the aquifer media showed that the entire study area had a high rate in the aquifer media, which is indicative of sandy sediments along with small amounts of clay and silt. The soil has often coarse grains in the study area. Most of the study areas, particularly the central areas, have a very low slope (0-2 percent). Therefore, in these areas pollutants that are combined with water have more chance of penetrating to lower areas. However, most of the border areas (12.2%) and small parts of the south areas (0.5% of the study area) have a slope of more than 12%. The vadose zone is affected by groundwater depth, and previous studies showed that the material at the upper part of the surface is mostly coarse. In this study, the land use map that was prepared via remote sensing technique was used to study the status of vegetation cover on the ground surface. Permeability corresponds to the vegetation status. Urban areas have a very low permeability, while forest areas and agricultural lands have a higher permeability due to their soil. The type and number of classes in the preparation of land use layer according to the initial purpose of the project, which specifies the area of land use within the study area, was classified into five classes including urban areas (4%), lakes and seas (0.36%), forests (1.36%), agricultural areas (47.5%), and arid land (46.78%).

The pollution vulnerability index is in the range of 98-168, which can be categorized into three classes. Accordingly, 57% of the study area had moderate pollution potential, 39.8% had high pollution potential, and 3.2% had very high pollution potential. The spatial analysis of this index showed that the southern parts of

 Table 1. Sensitivity analysis of SINTACS model by parameter removal method.

 Removed man
 S Min
 S Man
 S SD

Removed map	S-Min	S-Mean	S-Max	S-SD
S	1.11	0.34	0.15	0.50
Ι	1.60	1.83	1.93	0.17
N	1.60	0.95	1.04	0.35
Т	1.49	0.67	0.73	0.45
А	2.85	1.26	0.62	1.15
С	0.44	0.007	0.15	0.22
S	1.11	0.48	1.51	0.52

Where: S – groundwater level, I - impact of vadose zone, N -Net recharge, T - topography, A - Aquifer media, C - hydraulic conductivity, S – soil texture



Fig. 3. Map of SINTACS model for Ardabil aquifer.

the study area have moderate pollution vulnerability, and the northern areas have high and very high pollution vulnerability. The areas with high pollution vulnerability are the places where river density is low, and exit possibility of pollutants from these parts is low as well, adjacent to urban and rural areas, and the possibility of leakage from pollutants to these areas is high, as well as these being flat areas so pollutants have more time to penetrate. Besides, geomorphologic maps showed that the material in these areas is more alluvial. and surface soil mainly consists of sand, all of which caused a high pollution vulnerability in these areas. Majandang and Sarapirome categorized the SINTACS index into six classes (very high to very low), of which 45.54% had high vulnerability, 21.59% had moderate vulnerability, and 32.87% had low and very low vulnerability [44]. The researchers have stated that high vulnerability in some studied areas is due to coarse grain soil and its high permeability as well as the close proximity of groundwater to the ground surface.

# Results of Groundwater Pollution Occurrence Probability

The risk map of nitrate and arsenic of groundwater in Ardabil aquifer is presented in Fig. 4a), which includes five classes: very low, low, moderate, high, and very high. A risk map of nitrate showed that 14.72% of the study area had high and very high pollution risk, 59.4% had low and very low pollution risk, and other areas had moderate pollution risk. The areas with moderate and high risk included the western and northern parts of the study area. Considering the land use map, we found that these areas are agricultural lands where the fertilizers containing nitrate are used and can be considered as the main source of nitrate pollution, which is consistent with the results of Sajedi-Hosseini et al. [26].

A groundwater arsenic risk map (Fig. 4b) showed that western and northern areas are at high risk. As mentioned earlier, the origin of arsenic in groundwater can be considered as natural processes such as erosion of bedrock or volcanic material and human activities such as the the addition of pesticides and herbicides containing arsenic. The areas in which the risk of arsenic pollution is high are considered to be those with agricultural uses, where natural pesticides and herbicides or fertilizers are used in high amounts. The results revealed that 35.33% of the study area is at high and very high risk, and other areas are at lower risk.

Via comparing arsenic and nitrate risk maps, it was observed that the areas with high pollution risk are the similar areas on both maps, which revealed that these areas are all agricultural lands according to the land use map. Qurat-ul-Ain et al. [45] have reported that pollution in groundwater in Lahore occurs in agricultural areas where fertilizers and pesticides are used in large amounts and can cause groundwater pollution in these areas via leaching to the soil. In this study, the geomorphology map of the study area



Fig. 4. Risk map of nitrate a) and arsenic (b) in groundwater of Ardabil aquifer.

depicted that the areas including high pollution risk are parts of agricultural lands, and alluvial formations are dominant, leading to high rates of penetration and leaching.

#### Conclusions

Maintaining groundwater quality is very important due to its high consumption in different sectors as well as costly and timely removal of pollution. In this regard, identifying areas susceptible to pollution is essential. In this study, the pollution risk of groundwater with arsenic and nitrate, which are considered as important pollutants, was investigated. For this purpose, concentrations of arsenic and nitrate were matched with the layers of recharge potential model, and then the prepared map was combined with a groundwater vulnerability model (SINTACS). The results showed that 14.72% of the study area had a high risk of nitrate, and 35.33% had high risk of arsenic. In order to control pollution in Ardabil aquifer, it is recommended to reduce the use of fertilizers containing nitrate and arsenic and run modern treatment systems. This is due to the fact that the method of sewage disposal involves the use of absorbent wells in this province.

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#### **Conflict of Interest**

The author declares no conflict of interest.

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