JCHR (2021) 11(4), 375-382

Journal of Chemical Health Risks

www.jchr.org

ORIGINAL ARTICLE

Pollution Assessment of Trace Metals in Ground Waters (Case Study: Meshgin Shahr County)

Nafiseh Rezapour Andabili[*1], Mahsa Safaripour[2]

[1]*PhD student, Environmental field (trend: assessment and land use planning), Malayer University, Malayer, Islamic Republic of Iran*

[2]*Assistant Professor, Department of Agriculture and Natural resources engineering, Payam Noor University,Tehran, Iran*

(Received: 24 June 2020 Accepted: 28 October 2020)

KEYWORDS

Pollution of trace metals;
Arc GIS software;
Kriging;
Ground waters;
Meshgin Shahr plain

ABSTRACT: In this research, the data of wells in operation, deep and semi-deep wells were studied for assessment of trace elements of wells in Meshgin Shahr plain zone. Digital data were obtained using Arc GIS software. Using systematic random selection method, 46 wells were considered as the statistical population. For preparing zoning maps, after investigating a spatial correlation among the observed values, feasibility of preparing the underlying maps was studied using geostatistics methods such as inverse square distance and Kriging methods. Findings of the study indicated presence of trace metals (zinc and copper) in water. Considering continued trend of pollution and limited amount of aquifers, it will have, certainly, various environmental risks in long term. Hence, qualitative and quantitative protection and preventing increasing pollution of water, due to limited water resources in Meshgin Shahr plain, are among the main principles of planning in line with population and industrial development and excessive exploitation of Meshgin Shahr plain aquifer should be considered as the main factor in generation of chemical pollution. Findings of the study indicated that there is a significant difference between concentration of zinc and copper elements in the studied well waters. The highest average concentration is related to zinc element and the lowest concentration of trace metal is related to copper. The main reasons of trace elements presence are maternal stones storage capacity and transferring it to the ground waters. The two elements of zinc and copper are above the related standards specially at the north part of the area. Although type of the lithology affects amount of silicate and non-silicate minerals and considering diversity of lithology and concentration of human activities and residence at the elevation aligned foothills and plain lands have caused human factors (using chemical fertilizers, detergents) they cause accumulative effects on the above mentioned elements.

INTRODUCTION

Ground waters pollution is considered as one of the most important environmental issues [1]. Ground waters are the only water supply resources for millions of people in the world and their pollution has major effects on human health, industrial activities, agriculture and environment [2]. One of the main groups of ground waters pollutants, which happens naturally or by human is rare and inconsiderable toxic elements. Trace elements have caused considerable changes in Biogeochemical cycles, each having special effect in the body of human beings [3].

*Corresponding author: hrezapoor76@gmail.com (N. Rezapour Andabili)
DOI: 10.22034/jchr.2020.1902942.1150

Trace metals might be found in sewages resulted from metal industries, mining exploration, battery manufacturing factories, alloy mills and metal melting factories. Such industries' sewages enter into the river and influence their quality. Hence, identification and assessment of concentration of different types of pollutants in such sewages seem necessary and this should be done before their entrance to the flowing waters. Recent studies have shown that concentration of trace elements in water resources has destructive effects. Water and soil pollution to toxic cationic metals, results in lower function and quality of the product, encountering stability of agricultural production and people's health with serious dangers [4]. Some of the toxic cation metals are easily absorbed into the plant root, causing its toxicity. Some of the elements such as copper and zinc are necessary in lower concentration and poisonous at higher concentration [5].

Toxicity of trace elements such as copper, zinc, lead, … are found in different compounds of water. These elements have accumulative feature in the plants' texture, entering into human's food chain [6]. [7] In studying quality of ground waters quality in Trifa agricultural plains of Morocco in terms of ammonium nitrate and bacteriological pollutions employed ordinary Kriging method for examining and zoning qualitative maps of ground waters. [8] Used Kriging and simulation methods in order to prepare risks of nitrate in Madtay of Italy. Results of the investigation indicated that Kriging method is good for studying changes in the quality of ground waters. [9] To study superficial and internal assessment in Kam estuarine sediments (Heifong state in Vietnam) pollution to trace metals and arsenic, it was identified that economic, social, industrial developments and agricultural activities in the area have resulted in considerable pollution to cobalt, chrome, copper, manganese, nickel, lead, zinc and arsenic trace metals. In a research [10] titled as "Risk of Trace Metals Reception by Water to Human Health" chrome, copper, manganese, nickel and zinc metals were identified in 50% of 100 selected samples. Nickel and arsenic concentration in more than 20% and 58% of the samples was in accordance with the related standards. Findings of [11] indicated that zinc and copper elements amount in ground waters of central Gilan is lower than the presented standard for agricultural and drinking uses and cadmium and lead concentration is higher than standard values in most regions of the study area. Considering zoning maps of lead and cadmium elements, some areas have pollution of more than permitted limit, hence it is proposed to prevent digging new wells in the area and water of in operation wells in the area to be eliminated from residences' drinking and agricultural use system. The highest pollution is in Rasht county zone. Lack of sewage system in Rasht industrial town and surrounding cities might be one of the main reasons of ground waters pollution in the study area. It is proposed to take the necessary steps in acceleration of completing and operating sewage network of the city. It is, also, proposed to establish a permanent monitoring network for investigation of quality of ground waters in the study area, where in addition to anions and cations, trace metals should be taken into account, too. [12] Proceeded on investigation of concentration of trace metals in Zayandehrood river sediments and they concluded that cadmium amount in the sediments is worrying. [13] Conducted a research in Rafsanjan plain and concluded that the pollution of some parts of the study area with arsenic, lead and cadmium has natural and humanistic origins. They proposed that experiments on soil texture to be conducted for determination of the exact resource of the pollution. Considering lack of water problem in Rafsanjan plain, it is necessary to pay special attention to the pollutions identified in the research and take necessary measures for solving them. The aim of the present research study is estimation of trace metals amount in ground waters and zoning degree of pollution in Meshgin Shahr plain and finally developing practical solutions in line with improvement of the environmental conditions and the area's water condition, in particular.

The study area

Khiyav or Meshgin Shahr with an area of about 3880 square km (51 km length and 30km width) is the second largest city of Ardebil province. Meshgin Shahr county is bounded to Moghan county from North, Sabalan mountain

range from South, Ardebil county and Azerbaijan country from East and Ahar city of East Azerbaijan province from West. It has been located at geographical coordinates of 38^0 and 23' and 34" northern width and 47^0, 1' and 7" of Eastern length. Average height of Meshgin Shahr County is 1830 from free sea level. Figure 1 shows Meshgin Shahr county's geographical location in the province and country. According to the latest local divisions, Meshgin Shahr county involves three cities of Meshgin Shahr,Lahrood and Razi, 311 villages in 12 rural districts including three districts of Markazi, Arshag and Eastern Meshgin. The county has been located at 295km of Tabriz from Ardebil road and 168km of Tabriz from Ahar road. The study area involves Meshgin Shahr plain, which is influenced by topographic conditions such as heights, lands slope, lithological minerals of the region, erosion and sedimentology and finally human activities and ground waters are influenced by these features and activities, accordingly. Ground water of Meshgin Shahr plain is naturally and mostly influenced by penetration of snow melting waters at Sabalan heights both quantitatively and qualitatively. Human activities in Meshgin Shahr plain changes natural storage amount or penetration of trace elements in lithology minerals and also lead, zinc and copper in the ground waters. Hence, considering concentration of residential centers in Meshgin Shahr plain and effects of ground waters pollution on peoples' health and the agricultural productions, it is necessary to study the issue in details. The two investigated pollutants (i.e. zinc and copper) in the study area are compatible with development and natural and humanistic observable potentials due to its special topographic condition (about 3600 m difference), which has resulted in various land uses in the area, lithological condition of the area, which has diversity in terms of trace metals and also human presence and various activities, which are signs of increased pollutants in the ground waters of the area.

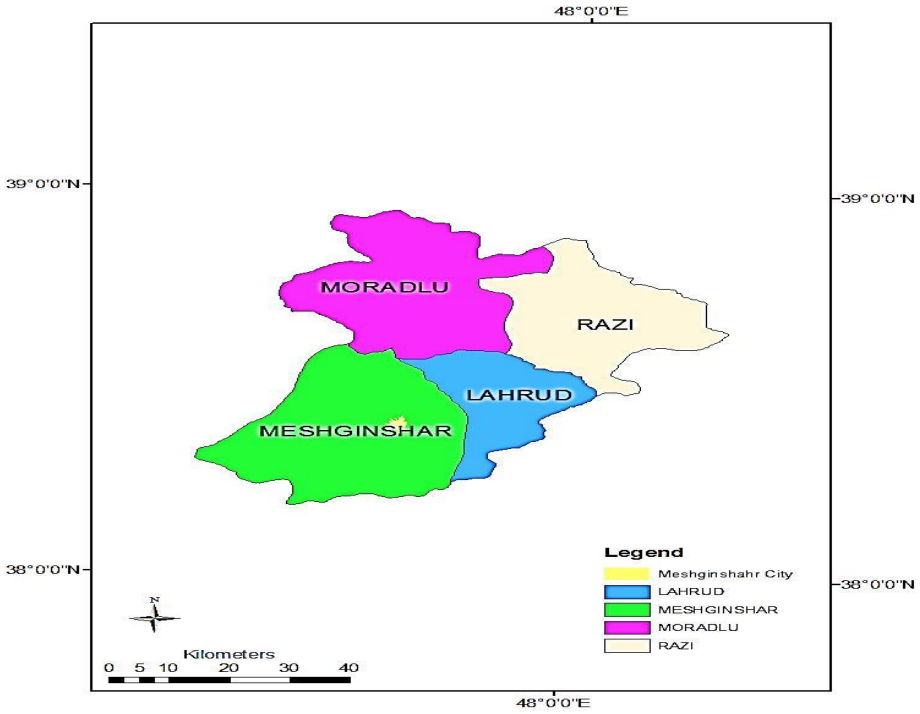

Figure 1. Geographical location of Meshgin Shahr County in the Province

MATERIALS AND METHODS

In this research the data of wells in operation, deep and semi-deep wells were studied for assessment of trace elements of wells in Meshgin Shahr plain zone. Digital data were obtained using Arc GIS software. Using systematic random selection method, 46 wells were considered as the statistical population. It is worth mentioning that these wells were introduced by Regional Water Company of Ardebil Province as the ground waters qualitative monitoring network, indicating ground water reservoirs' qualitative condition in the study area. For preparing zoning maps and determining elements concentration values, after investigating a spatial correlation among the observed values, feasibility of preparing the underlying maps was studied using geostatistical methods such as inverse square distance and Kriging methods.

Spatial changes pattern and spatial continuity degree of the variables were assessed by variogram in the kriging method. Hence, first the experimental variogram was calculated using the equation 1 and then based on criteria of the R2 coefficient of determination and total remaining squares (RSS), one of the round, linear, Gaussian or exponential variograms was fit into experimental variogram [14].

$$Y(h)=1/2N(h)£\{z(x_i)-z(x_{i+h}\}^2 \quad (1)$$

Where: $\gamma(h)$ is variogram: h is step, N is number of pair observations, Z_{xi} and $Z_{(x+h)}$ is the observation value of the variables at the base point of inverse distance weighting method. Weighing is based on inverse distance to estimation point. In other words more weight is given to the closest samples and lower weight is given to the samples which are farther.

Interpolation methods assessment in this study was conducted based on the two standards of Mean Absolute Error (MAE) and Mean Bias Error (MBE), in a way that from among above mentioned methods, the method with smaller MAE was selected as the most appropriate method for generalization of the results to other unsampled points and for drawing the maps. MAE shows the method's accuracy and average error value, which is better as it is closer to zero. MBE is a standard of bias in the estimated data. It's closeness to zero shows unbiased estimations [15].

Using Kolmogrov-Smirnoff test [16], it was identified that the data of zinc and copper elements follow non-normal distribution. Considering the importance of normal data condition in Kriging method logarithm conversion with natural base was used, for zinc and copper elements.

Topography map of the study area, on which the wells' condition has also been added was used as a research instrument and GPS was used to investigate and improve location of surface effects and wells.

Revisiting after zoning of pollution degree in order to investigate effects of trace metals including zinc and copper in order to present some solutions and decreasing the effects in the region.

Data analysis statistical methods

Considering the importance of ground water in supplying needed water of different uses in the plain, the issue of investigating chemical pollutant resources and the pollutants related to the identified ground waters including zinc and copper enjoys higher level of importance. Hence, in this study in line with investigation of pollution caused by trace metals, considering statistical population and size in the field of number of samplings and graphical statistical analysis in GIS and digital investigations in Excell, firstly the available experimental data were entered into the software, then through statistical program writing, they were analyzed in ratio of statistical parameters and SPSS was used for normalization of some data, described in the following section.

One of the main conditions of using Geostatistics technique for interpolation is that the used data should follow normal distribution. Hence, before zoning the measured elements their normality is examined by parameters such as Skewness and kurtosis and also Kolmogrov-Smirnoff test.

RESULTS

Summary of the statistical condition of some of the chemical and physical features of soil: dominant soil texture of the area is loamy based on the area's geological logos in terms of soil classification. Capacity is an important factor in mobility and non-mobility processes of the trace metals in soil and water. This issue is resulted from changes of organic material and clay percent in the soil considering use type, geological formations and path of surface waters in ratio of the pollutants, which appears, gradually, in distribution of trace metals concentration in ground waters. Electrical conductance and soil PH of the study area has higher diversity due to lithological diversity and soil chemical features, accordingly, so that the minimum PH of the soil is 6.35, which is neutral tending to acidic form. This can be observed in lands of Doost Beiglu village and at the center of the study area. Maximum PH (8.9) is seen in Balucheh Mirak located at the southern corner of Meshgin Shahr County. Moreover, electrical conductance of the studied samples in the study area is low salinity on average ($\mu s.cm^{-1}$895).

Estimation of background concentration

Maternal materials are one of the most important resources of trace elements entrance into the soil. [17] mentioned that the elements concentration is gradually decreased in ratio of the bed rock with soil building processes and weathering the bed rock. Generally, since sandstones are mainly made of quartz, so they have less concentration of the metals in them; this is while clay sediments and shales can have higher amounts of such metals in them due to their higher ability in absorbing metal ions. The materials derived from weathering of coarse rained stones such as rhyolite and granite have less amount of elements such as copper, zinc and cobalt compared to fine grain materials such as shale and basic igneous stones [18]. Monzonite penetrating masses, Monsonite quartz and their related thermal fluids enjoy mineralization of copper and lead elements type. Rhyolite, dacite and andesite and basalt domes, which are younger than Oligocene, bear less weathering and the mineralization was in tourmaline form in tourmaline.

The highest change coefficient of copper and zinc concentration in the study area is related to zinc element. In this study the geometric mean concentration of surface soil trace metals in the upstream region (natural lands) and downstream region (including farm lands and urban areas)

were considered as natural background concentration and human background concentration, respectively. As it can be seen in the equation 1 Geomtric Mean (GM) of natural logarithm mean is a set of data (x^1, x^2, … x^n), which is finally retrieved by exponential conversion [19].

$$GM= Ln_x \sum n_i=1 /n \exp$$

To study concentration rate of the trace metal in a variable, it is necessary to be aware of their amount in different stones.

Hence the trace metals studied in different types of stones have been presented in the table 1 and this might cause better resulting in the environments containing higher concentration of such metals.

Table 1. Average trace metals in different types of stones. Data obtained in ratio of ppm [20]

Elements environment	Earth crust	Igneous rocks			Sediment stones		
		Ultramafic	Mafic	Granite	Limestone	Sandstone	Shale
Zn	75	58	100	52	20	30	120
Cu	50	42	90	13	5.5	30	30

Zoning pollution degree of trace metals elements in Meshgin Shahr area

Investigation of zinc and copper elements in Meshgin Shahr county indicates that industry type, mining, soil science, lithology and land use have been developed in accordance with features of each element, so that north part of the study area with Limestone and metamorphic rocks PH is high and the land use is agricultural and normal pasture, zinc can be found more than copper and at the center of the county, which has agricultural land use, sand and loamy soil with alluvial stones, copper amount is more than zinc and at the south part of the county, which has volcanic rocks with land use of dense pasture and thin forest, zinc amount is more than copper. According to the overlapping of the elements studied in Meshgin Shahr county and considering the above mentioned issues and studying figure 2 it is concluded that the highest density of pollutant elements are the center of the county drawn from lands of Davacho Oliya toward east to the lands of Garapey Oliya, which have land use of rain-fed agriculture and this area has been drawn toward Jabarlu village lands , to some extent and a limited spot is observed at the West part of Khorde Qishlaq village. The highest level of elements pollution zoning is related to zinc and copper with average pollution, so that the highest level of pollution is seen at south and center of the county. On the other hand, at the south part of the county Toof and Lahar rock layers show lower storage capacity of trace metals elements and in terms of the study elements pollution level, it is at unpolluted to average pollution.

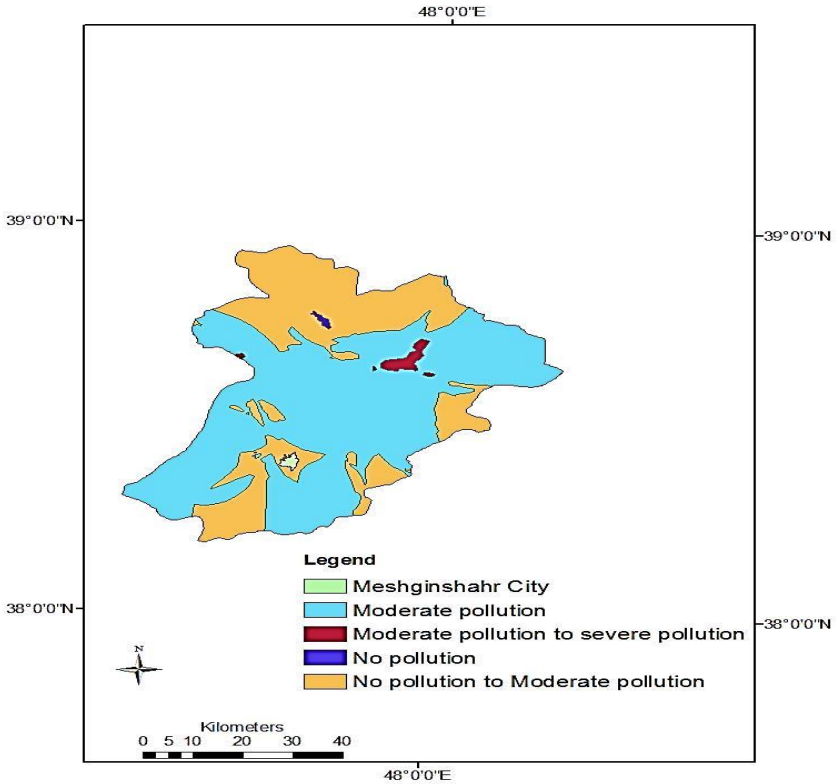

Figure 2. Zoning pollution rate of trace metals in Meshgin Shahr County

DISCUSSION

In a research [21] they determine the groundwater suitability for drinking use based on trace metal concentration and the associated human exposure risk in an intensively irrigated part of the Cauvery river basin, Tamil Nadu, India. Sixteen trace metals analysed were in the order of dominance ofchromium < zinc < copper < cadmium < cobalt < iron < aluminium < nickel < titanium < zirconium < boron < silver < manganese < lead < lithium < silicon in groundwater. Results of the study indicated that there is a significant difference between concentration of zinc and copper elements in the study wells, so that the highest average concentration is for zinc element (ppm 121/4) and the lowest trace metal concentration is related to copper (ppm 8/3). The investigations indicated that the main reason of trace metals are storage capacity of the maternal stones and transferring it into the ground water. So that PH rate is lower in the southern lands of the county among lands of Arablu, Qarbaghlar and lands of Dastir village, compared to other area (7-6/4). And the western corner of the county to the lands of Dostbeiglu village has PH rate of (7-7.5). This region land use is low dense to average dense pastures and in term of lithology it is among young alluvial terraces and the western corner's lands has stones of old alluvial terraces, which has the lowest potential in providing conditions for zinc building in the study area. On the other hand the highest level of PH at the northern corner of the county is 8.5-9, which begins from Mazafa village and extends to the lands of Seyyed Javadlu village. Considering that the main land use of the area is average pasture, rain-fed agriculture and gardens to some extent, it can be found that the area has higher amount of Humos from soil science perspective and in terms of limestone lithology it has higher storage capacity of zinc. It has also metaphoric rocks with silicate minerals, so that formation complex of copper, zinc, gold, and arsenic and lead is composed of metaphoric rocks alterations. In the western zone and heights of the study area, the major land use is average pasture and its rocks are among igneous stones. And silicate minerals are mostly observed in it and iron and alloy minerals are among its dominant elements. In other parts specially central part of the county, although PH is neutral with sedimentation rocks such as alluvial terraces and the capabilities of the hill lands is mostly sand stone, clay and igneous, so that with increase of height igneous stones surfaces increase and their land use is mostly rain-fed agricultural lands and pastures. Considering intense limitation of water resources in Meshgin Shahr plain, it is necessary to take appropriate management steps of the plain aquifer for appropriate location for establishing future developmental uses such as industrial development, agriculture and human communities. Considering harms of using chemical fertilizers and pesticides, controlling use of them and using new methods of fighting plant pests seem necessary.

ACKNOWLEDGEMENTS

The authors gratefully would like to thank Research Council of Malayer University and anonymous referees who kindly improve the paper by their valuable comments.

Conflict of interests

The authors declare that there is no conflict of interest.

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